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Full Name of Author — Nom complet de l'auteur

PETER SCHVAN

Date of Birth — Date de naissance

28 March 1952

Country of Birth — Lieu de naissance

HUNGARY

Permanent Address — Résidence fixe

330 Driveway Apt 806
OTTAWA, ONT K1S 3M9

Title of Thesis — Titre de la thèse

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Name of Supervisor — Nom du directeur de thèse

Professor R. E. Thomas

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CW LASER-INDUCED DIFFUSION
IN SILICON

by

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This report is a thesis submitted to the
Faculty of Graduate Studies and Research
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Department of Electronics
Faculty of Engineering
Carleton University
Ottawa, Canada
November 1984

The undersigned recommend to the Faculty of Graduate Studies and
Research the acceptance of the thesis:

"CW Laser-Induced Diffusion in Silicon"

submitted by Peter Schvan in partial fulfillment of the
requirements for the degree of Doctor of Philosophy.

Prof. R. E. Thomas
Thesis Supervisor

Prof. M. A. Copeland
Chairman
Department of Electronics

Dr. D. F. Williams, NRC
External Examiner

January 2, 1985

ABSTRACT

This report describes a novel technique to form shallow p-n junctions in silicon using a cw argon laser. The process is based on the rapid localized melting of the silicon surface by the laser beam to induce liquid phase diffusion from a deposited source.

Laser heating of silicon is investigated by calculating the time evolution of the temperature profile including the effects of phase transition using computer simulation. This time-dependent analysis, which is capable of predicting the dependence of the maximum melt depth on the incident laser power and scan speed, is used to design the cw laser processing experiments.

Considerations to minimize laser-induced crystal damage and the significance of high scan speed along with the design of the beam scanner are discussed. The fabrication of junction diodes using the cw laser-induced diffusion technique is described, including the deposition of a phosphosilicate glass diffusion source which allows selective processing, and the application of tungsten silicide to form reliable contacts.

Finally, experimental results on the electrical behavior of p-n junctions formed by this technique are discussed. Good diode characteristics with breakdown voltages over 35 V and leakage currents around 5×10^{-6} A/cm² have been obtained demonstrating the feasibility of this method.

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LIST OF SYMBOLS AND ABBREVIATIONS

$\alpha, \alpha(z)$	optical absorption coefficient,	cm^{-1}
AR	antireflective	
C_{AUG}	Auger recombination coefficient, 4×10^{-34}	cm^6/s
C	capacitance	F
C_L	energy transfer rate constant, 10^{11}	eV/s
C_{OX}	phosphorus concentration in the SiO_2	cm^{-3}
C_{OX}^0	original phosphorus concentration	cm^{-3}
CPU	Central Processing Unit	
cy	heat capacitance	J/gK
C-V	capacitance vs. voltage	
CVD	Chemical Vapor Deposition	
cw	continuous wave	
d	wafer thickness	cm
d_b	laser beam diameter	cm
d_0	thickness of antireflective layer	cm
DI	di-ionized	
D	thermal diffusivity	cm^2/s
D_A	ambipolar diffusivity	cm^2/Vs
D_L	liquid phase diffusivity of P in Si	cm^2/s
D_{OX}	phosphorus diffusivity in SiO_2	cm^2/s
e	natural logarithm base, 2.718	
E_{ABS}	absorbed laser power density	$\text{Jcm}^{-3}\text{s}^{-1}$
E_{CAR}	energy density of excited carriers	Jcm^{-3}

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

E_{PHOT}	photon energy, approx. 2.5	eV
f	focal length of lens	cm
F_i	function based on finite differences	
ϕ	angle of bevel	
G	function based on finite differences	
h	time step	sec.
H	heat energy density	Jcm^{-3}
H_F	latent heat of fusion for silicon	Jcm^{-3}
H_L	second derivative of $H(r)$	Jcm^{-5}
i	imaginary unit	
I_L	leakage current	Acm^{-2}
$I-V$	current vs. voltage	
$I(x,y)$	laser beam intensity distribution	Wcm^{-2}
IR	infra-red	
J	current density	Acm^{-2}
J_s	saturation current density	Acm^{-2}
k	Boltzmann's constant, 1.380×10^{-23}	J/K
$k(T)$	thermal conductivity	W/cmK
$L, L(z)$	lateral diffusion	Kcm^{-2}
λ	wavelength	cm
n	diode quality factor	
n_1, n_2, n_3	refractive indices	

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

N	number of grid points	
N_e	electron concentration	cm^{-3}
N_0	equilibrium electron concentration	cm^{-3}
π	constant, 3.14159	
P	laser power	W
PSG	Phosphosilicate Glass	
q	electron charge, 1.602×10^{-19}	C
r	radial distance in cylindrical coordinate system	cm
r_1	radius of the molten puddle	cm
r_{12}, r_{23}	ratios of refractive indices	
R, R(T)	reflectivity	
RBS	Rutherford Backscattering	
RF	radio frequency	
ρ	density	gcm^{-3}
s	thermal diffusion length	cm
S	heat source	Wcm^{-3}
SIMS	Secondary Ion Mass Spectroscopy	
t	time	sec.
T, T(z)	temperature	K
T_B	backsurface temperature	K
T_e	carrier gas temperature	K
TEM	Transmission Electron Microscopy	

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

T_i	temperature at the i -th grid point	K
T_L	lattice temperature	K
T_M	melting point of silicon, 1690	K
t_r	thermal response time	sec.
T_z	temperature along the z axis	K
T_0	reference temperature	K
θ	unit step function	
UV	ultra-violet	
x, y	distance in Cartesian coordinate system	cm
x_j	junction depth	cm
z	distance in cylindrical coordinate system	cm
V	voltage	V
VLSI	Very Large Scale Integration	
$w, w(z)$	$1/e$ laser beam radius	cm
w_0	minimum spot size	cm

CHAPTER 1

INTRODUCTION

1.1 General Introduction

The utilization of high energy laser beams in semiconductor technology has become a rapidly growing field during the last few years after its first reported application [1,2] in the mid 1970's. The large number of papers [3-6] leaves little doubt that this novel technique will soon become, if it is not already, a standard process in semiconductor manufacturing laboratories.

The laser beam processing technique has great potential for advancing the state-of-the-art in fabrication of semiconductor devices and integrated circuits. The unique characteristics of this technique due to its ability to heat a spatially localized region to a high temperature for a short period of time, opens up various possibilities of microelectronics device fabrication that are novel and could prove to be essential for the realization of very large scale and/or very high speed integrated circuits.

At Carleton University the research in this area was initiated by S. Mukherjee and Professor R.E. Thomas in 1979. After the purchase of a CR-18 cw argon ion laser successful experiments were

carried out to recrystallize amorphous and polycrystalline silicon [7,8]. The author of this report joined the research group in the fall of 1980 as a visiting researcher and carried out initial experiments on Schottky diode formation. In early 1982 the research moved in a new direction the result of which will be presented in this report.

The continuing trend of the scaling down of device dimensions, which is an integral part of VLSI design, requires shallower junctions, higher doping levels and reduced defect density. The inadequacy of standard furnace annealing to achieve these goals has motivated this research to develop a new technique using laser beam processing. Thus, the aim of this work is to investigate the feasibility of using cw argon laser annealing as an alternative processing technique to form p-n junctions through laser-induced diffusion.

This chapter reviews the main characteristics of the short time annealing technique and its applications, with special attention paid to previous work on laser-induced diffusion.

1.2 Review of Short Time Annealing

Short time annealing encompasses a wide range of processing techniques which can thermally process materials over an extremely

wide range of times, 10^{-8} to 10^2 s, all short compared to standard furnace annealing. Laser annealing represents one of these techniques. A brief comparison of the various possibilities will be presented to introduce the basic concepts and point out the different problems involved in using these techniques.

The main characteristics of an annealing process depend on the mode of energy transfer from the source to the sample which can include laser light, incoherent light, electron beam or black body radiation from a resistance heater. The absorption depth for visible wavelengths as well as electrons at 10-30 KeV are within 0.01-2 μm . The most important difference between these sources is how the time period in which the energy is delivered compares to the thermal response time, t_r , of silicon where $t_r = s^2/D$, s is the thermal diffusion length or sample dimension. Using the thermal diffusivity of silicon, D , close to the melting point, a simple calculation shows that it takes 5 μs and 3 ms for the heat to diffuse 10 μm (the extended junction depth) and 250 μm (the wafer thickness) respectively.

Table 1.1 compares the important characteristics of major annealing techniques. For a pulsed energy source where the dwell time is short, (<100 ns) compared to t_r , the system behaves adiabatically. Pulsed laser studies usually employ Q switched ruby or Nd:YAG and recently eximer lasers, with a beam diameter in the order of 1 cm. In this adiabatic process pulses 10-100 ns long and

	Time	Type of process	Possible crystal damage
furnace	1 min - 10 hr	solid phase isothermal	wafer warpage
resistance heater, lamp	1 s - 1 min		
cw laser or e-beam	0.1 ms - 1 ms	solid phase non-isothermal	slip dislocation point defects
pulsed laser or e-beam	1 ns - 100 ns	liquid phase adiabatic non-equilibrium	ripples dislocation point defects

Table 1.1 Comparison of different annealing techniques.

with energies of about 1 J/cm^2 will melt the silicon surface resulting in a liquid phase process [9,10]. Since the diffusion of heat is limited during this short time period the temperature rise is extremely rapid generating large spatial thermal gradients which can cause dislocation formation. The fast cooling rate results in a nonequilibrium situation posing long time reliability problems. Another problem is the nonuniformity of the beam which, however, has been improved by different beam homogenization techniques.

In cw laser annealing studies argon ion, Nd:YAG and, to a much lesser extent, CO₂ lasers have been used. The beam is raster scanned over a large area with substantial overlapping. For the argon laser a spot size of 20-150 μm diameter with a scan speed of 1-10 cm/s represents a typical experimental condition. Since the corresponding dwell time is between the time for heat to diffuse to the extended junction depth and to the wafer thickness, thermal diffusion during annealing will affect significantly the resultant temperature profile. Consequently cw laser annealing is characterized by a slower temperature rise and cooling rate than for pulsed annealing, and also smaller temperature gradients and induced stress. At sufficiently high laser power the silicon melts. In most reported experiments, however, power levels around 75% of the power needed for melting have been used, generating only solid phase processes [11-13].

The latest approaches to short time annealing use a variety of light sources, halogen lamps, arc lamps and radiating resistance

heaters, acting as line or area energy sources, to heat the sample for 1-100 s. The relatively long annealing times, (longer than the thermal response time of the wafer) and the large heat sources result in an isothermal annealing condition with uniform temperature distribution. While offering advantages in several applications, these approaches are not suitable for localized selective processing or to induce liquid phase processes.

1.3 Review of Applications

The first area where short time annealing, using a laser energy source, has been employed is the annealing of ion implanted single-crystal silicon substrates [14-16]. The purpose in this case is to remove lattice damage and electrically activate the dopants without significantly altering the impurity profile. Both pulsed and cw lasers have been used successfully to achieve these goals. The dramatic discovery that the damaged silicon layer can be regrown to a high level of crystal perfection by both liquid and solid phase epitaxy initiated the study of the recrystallization of polycrystalline and amorphous silicon. The recrystallized layer formed on top of an insulating layer can then be used as a starting material for further device fabrication [17-19].

A large number of other applications have since emerged. The

formation of a p-n junction by means of laser-induced diffusion represents the topic of this report and will be reviewed in greater detail. Other applications include: metal-silicide formation to lower the resistance of interconnections and prepare reliable contacts [20-25], chemical vapor deposition [26-28], back surface gettering, and etching for maskless fabrication [29].

1.3.1 Laser-Induced Diffusion

The doping of materials via laser-induced diffusion, which consists of the deposition of the desired impurity on the surface followed by irradiation with a high energy laser beam, is an attractive alternative to ion implantation or conventional thermal diffusion, because (a) it is a simpler process (b) it offers the possibility of selective processing and (c) it allows the incorporation of a dopant over its solid solubility limit coupled with 100% electrical activation. This technique also allows the formation of very shallow junctions difficult to achieve by other methods.

It is important to point out that the introduction of dopants into a substrate material by thermal processing within a time period shorter than 10 ms can only be carried out through liquid phase diffusion or mixing [30-32]. This becomes evident if we compare the diffusivity of major dopants (Table 1.2) at temperatures below the

Impurity elements	Diffusion coefficient in liquid silicon (cm ² /s)	Diffusion coefficient in solid silicon at the melting point (cm ² /s)
B	2.4×10^{-4}	1.0×10^{-10}
Al	7.0×10^{-4}	4.0×10^{-10}
Ga	4.8×10^{-4}	1.4×10^{-10}
In	6.9×10^{-4}	5.5×10^{-11}
P	5.1×10^{-4}	1.0×10^{-10}
As	3.3×10^{-4}	1.0×10^{-11}
Sb	1.5×10^{-4}	1.3×10^{-11}

Table 1.2 Diffusion coefficients of impurities in sil

melting point and in liquid silicon [33-34]. Solid phase processes can not produce an appreciable amount of diffusion within such a short period of time due to the several orders of magnitude lower diffusivity for impurities. The process must include (a) the melting of a thin surface layer (b) the fast liquid phase diffusion of the dopant followed by (c) an epitaxial regrowth of the molten layer.

Since melting is usually carried out by a pulsed laser, most of the experiments on laser-induced diffusion have also used this approach. One explanation for this is that melting with a cw laser would result in an excessive liquid flow (as will be discussed later) during the longer dwell times typically used, leading to an intolerable disturbance of the semiconductor surface.

Table 1.3 summarizes the published experimental work on the formation of junctions via laser-induced diffusion.

The laser-induced diffusion technique was proposed many years ago for the diffusion of phosphorus [35] and aluminum [36]. At that time, however, the junctions formed were of small area and exhibited poor electrical characteristics mainly because of the damage created by the high energy pulsed laser used. Since then a variety of experiments have been carried out using different diffusion sources and annealing conditions.

Schottky barrier junctions were prepared by alloying vacuum

DOPANTS/ SUBSTRATE	LASER PARAMETERS	JUNCTION CHARACTERISTICS	REFERENCES
paint-on P/Si	ruby, 2×10^{-3} - 2×10^{-1} J/cm ²	n=1.8 I _L = "moderately high"	Fairfield ... [35], 1968
evaporated Al/Si	Nd:YAG 300 ns 0.2-3 mJ	n=2 I _L = "10 ³ x Si junction"	Harper ... [36], 1969
paint-on P,B/Si	Nd:YAG or CO ₂	NA	Affolter ... [41], 1978
evaporated B/Si	ruby, 50 ns 1.5-1.7 J/cm ²	n=1.39 x _j = 0.4 μm I _L = 5×10^{-7} A/cm ²	Narayan ... [39], 1978
evaporated Al/Si Mg/GaAs	ruby, 40 ns 1.5 J/cm ² 0.7 J/cm ²	n=1.2 I _L = 10^{-7} A/cm ² I _L = "large"	Young ... [37], 1979
evaporated P,Sb,Al,Ga, Bi,In /Si	ruby, 20 ns 1.5 J/cm ²	x _j < 0.4 μm n=1.75-2.2 I _L = 5×10^{-6} A/cm ²	Fogarassy ... [40], 1980
ion impl. As,P/Si	cw Ar ion 1 s, 40 μm	NA	Matsumoto ... [44], 1980
spin-on Sn/GaAs	cw Ar ion 12cm/s; 50 μm 0.6 and 1 W	NA	Nissim ... [45], 1980
liquid P,Sb/Si	ruby, 20 ns 1.1-2 J/cm ²	n=2 I _L = 10^{-3} A/cm ²	Stuck ... [42], 1981
evaporated Al/Si	cw Ar ion 2cm/s; 50 μm 12-22 W	n=1.26-2 I _L = 10^{-3} - 5×10^{-5} A/cm ²	Wu ... [38], 1981
evaporated Pt/Sb/Si	cw Ar ion 12W Nd:YAG 5 J/cm ² 4 cm/a; 40 μm	n=1.8-2 I _L = 10^{-4} A/cm ² "moderately good diodes"	Schutz ... [47], 1982

Table 1.3 Published laser-induced diffusion experiments.

Laser processing parameters: time = dwell time; distance = beam diameter; velocity = scanning speed;

Lasers were used in pulsed mode unless stated otherwise.

evaporated Al film into n-type Si. In this case the formation of an Al-Si eutectic that results in the melting of the Al-Si interface coupled with Al diffusion accounts for the observed Al/p⁺-Si/n-Si structure. This junction exhibits large barrier height and good rectifying characteristics [37,38].

P-n junctions were also fabricated using vacuum deposited dopants such as boron, phosphorus, antimony, etc. [39,40], paint on sources [41], and liquid sources [42]. All of these experiments used pulsed lasers to melt the surface layer producing in some cases diodes of good quality. The application of this technique has so far been restricted to solar cell fabrication, where the resultant high surface concentration which is often above the solid solubility limit [40] coupled with a shallow junction depth, makes it an inexpensive method to prepare high efficiency solar cells [43].

Experiments on cw laser-induced diffusion are scarce. Solid state diffusion was studied by annealing ion implanted arsenic and phosphorus in silicon [44]. In this case 1000 scan frames were required to achieve a long enough dwell time (1 sec) necessary to produce measureable diffusion at temperatures in the vicinity of the melting point. Since it would take several days to process a full wafer this cannot be considered a viable approach.

In another experiment the diffusion of tin into GaAs was initiated by high temperature heat treatment prior to cw laser annealing [45]. Al/n-Si Schottky diodes were also formed using a cw

laser [38,46].

Recently p-n junctions with Pt silicide contact were formed by melting a Pt/Sb/p-Si composite thin film structure by using either scanned cw or pulsed lasers [47]. The probable explanation for the diode behavior is that during the regrowth from the melt some Sb remained in the regrown Si layer which is deeper than the Pt-silicide layer, leading to a p-Si/n⁺-Si/Pt-silicide structure.

1.4 Objective and Thesis Outline

The objective of work described in this thesis is to develop a process, using the cw laser-induced diffusion technique, which is suitable for producing good quality shallow junctions for microelectronics applications.

A new approach will be described which employs a cw argon ion laser beam scanned at a high speed to melt the silicon surface in order to induce liquid phase diffusion. A phosphosilicate glass layer deposited at low temperature is used to serve as a diffusion source and also to act as an antireflective coat. This new technique provides good control over the maximum temperature rise and melt depth and also suppresses liquid flow so that for the first time good quality p-n junctions can be produced by the cw laser-induced liquid phase process.

Since the high speed scanning of the beam results in a dwell time which is on the order of the thermal response time of the extended junction depth, in this sense, this approach represents a technique which is between those using pulsed lasers and cw lasers scanned at low speeds (< 10 cm/s).

To investigate the temperature rise in silicon induced by a cw laser during a short period of time it is necessary to solve the time dependent heat flow equation including the effects of melting. Theoretical considerations on the heat transfer will be discussed in chapter 2. This is followed by the description of a novel numerical simulation of cw laser heating, developed to analyze the time evolution of the temperature rise, and the discussion of the results of this calculation in chapter 3.

The various considerations about laser induced damage, which led to the design of this cw laser processing technique, the description of a novel beam scanner, and the role of the phosphosilicate glass are the topics of chapter 4. Chapter 5 presents the experimental procedure developed to fabricate p-n junction diodes, including the deposition of phosphosilicate glass diffusion source, laser processing, and contact formation using tungsten silicide. The diodes formed have been tested using mainly electrical methods. The results of these measurements are discussed in chapter 6. Finally, chapter 7 concludes this report and makes suggestions for further work.

CHAPTER 2

THEORY OF LASER-INDUCED HEATING

Any process induced by the absorption of laser energy, whether it is a liquid or solid phase reaction, depends on the resultant time evolution of the temperature profile - a key parameter that ultimately determines the electrical characteristics of the laser processed semiconductor device. There are implications, however, that the laser induced reaction has nonthermal characteristics in the case of very short laser pulses [48]. However, this problem is beyond the scope of the present discussion.

Unfortunately it is very difficult to measure this temperature profile due to the relatively short period of time and the extremely steep spatial distribution involved. Although several techniques have been used they were either inaccurate [49] or involved very complex instrumentation and evaluation techniques such as Raman spectroscopy [50] or X-ray diffraction [51]. Because of the lack of a simple experimental technique it is necessary to resort to theoretical calculations which can predict the temperature rise as a function of laser beam parameters and material properties.

There are basically two problems that have to be addressed. The first is the energy coupling between the laser beam and the

solid [52,53] which ultimately determines the distribution of the energy absorption by the lattice. After that the time dependent heat diffusion problem has to be solved. The difficulties associated with these problems are two fold, viz., the complexity of the physical phenomena involved in the energy transfer, and the highly nonlinear nature of the heat equation due to the temperature dependence of the optical and thermal properties of silicon.

This chapter will discuss the physical processes involved with the absorption and the subsequent transport of energy with special attention to the temperature dependence of these processes, and will also review the existing heat flow calculations and their limitations.

2.1 Coupling of Beam Energy to Solids

Electromagnetic radiation with wavelengths ranging from UV to IR interacts exclusively with electrons. As a result of the excitation free electron-hole pairs are generated via indirect absorption processes in the case of silicon [52,54]. Free carrier absorption is negligible for electron concentrations less than 10^{20} cm^{-3} [55]. The distribution of the laser energy input is determined by the light absorption which is characterized by the absorption coefficient, α :

$$E_{ABS}(x,y,z) = \alpha(z) (1-R) I(x,y) \exp\left\{-\int_0^z \alpha(z') dz'\right\} \quad (2.1)$$

E. J. Yoffa examined the process by which the laser energy is transferred to the lattice [56]. She pointed out that excited carriers can diffuse away before releasing their energy to the lattice increasing the volume in which the energy is delivered to the lattice. The excited carriers thermalize with the rest of the carriers in a much shorter time period than the energy is transferred to the lattice, so the carrier temperature (T_e) is initially much higher than the lattice temperature (T_L). The other important parameter that characterizes the excited carrier gas is concentration.

The energy transfer processes can be described by using the continuity equations for the carrier energy and concentration:

$$\frac{\partial E_{CAR}}{\partial t} = \frac{\partial}{\partial z} \left(D_A \frac{E_{CAR}}{N_e} \frac{\partial N_e}{\partial z} \right) + E_{ABS} - C_L \left(1 - \frac{T_L}{T_e} \right) N_e \quad (2.2)$$

$$\frac{\partial N_e}{\partial t} = \frac{\partial}{\partial z} \left(D_A \frac{\partial N_e}{\partial z} \right) + \frac{E_{ABS}}{E_{PHOT}} + C_{AUG} N_e (N_0^2 - N_e^2) \quad (2.3)$$

The first terms represent the diffusion of the carriers. The last term in the energy balance equation (2.2) is the energy transfer rate to the lattice [57]. The constant C_L is in the order of 10^{11} eV/s.

The only important mechanism involved in the carrier recombination is the Auger process [54,58], which is characterized by a lifetime that depends on N_e^{-2} . This process does not result in the energy loss of the carrier system because the energy is taken up by a third carrier, C_{AUG} for silicon is $4 \times 10^{-34} \text{ cm}^6/\text{s}$.

Since all these processes are much faster than the temperature change during cw laser annealing, we can assume that the electron gas is always in steady state condition at a given temperature. Under this condition the carrier temperature and concentration can readily be calculated, yielding eventually the depth distribution of the lattice energy absorption.

Without having to go into the details of this calculation an important conclusion can immediately be drawn by comparing the order of magnitudes of the different terms in the equations. For pulsed laser annealing the rate of energy absorption is above $10^{34} \text{ eV/cm}^3\text{s}$ which results in a carrier temperature which is significantly higher than the lattice temperature. In the case of cw laser annealing, however, the energy absorption rate is only about $10^{28} \text{ eV/cm}^3\text{s}$, from which it follows that the carrier temperature remains close to the lattice temperature, while the concentration is above the equilibrium value. The reason behind it is that the carrier concentration does not increase proportionally with the laser energy due to the N_e^3 type dependence of the Auger process.

As a result, in the case of cw annealing the lattice and carrier

systems are energetically in equilibrium - the rate of energy transfer to the lattice is approximately equal to the rate of energy absorption by the carriers. Thus the laser energy is coupled to the lattice at the same site in which photons are absorbed, and (2.1) can be used as the energy source term for the calculation of temperature rise during laser annealing.

This result might be an explanation as to why cw laser annealing can be explained by thermal phenomena while pulsed laser annealing often exhibits non-thermal characteristics.

2.2 Temperature Dependent Optical and Thermal Properties of Silicon

During laser annealing the temperature of the solid can vary from room temperature to above the melting point resulting in significant change in the thermal and optical properties of the solid. The most dramatic change occurs during phase transition, crucially affecting the temperature rise. The validity of any temperature rise calculation depends on how precisely these variations are taken into account.

2.2.1 Heat Capacitance Density Product

The heat capacitance of silicon (cv) increases slowly with

temperature. The total variation, however, is only about 20% between 600K and 1800K changing from approximately 0.85 to 1.05 J/gK [59]. The density (ρ) on the other hand slightly decreases with temperature and only increases about 10% upon melting [60]. Because of this small variation the heat capacitance density product is very often taken to be constant or modeled by a slowly varying function throughout the whole temperature range [61].

$$c_p \rho = 2.335 \frac{T-159}{T-99} \text{ J/Kcm}^3 \quad (2.4)$$

2.2.2 Thermal Conductivity

The thermal conductivity changes significantly first by decreasing from the 1.5 W/cmK room temperature value to about 0.2 W/cmK at the melting point of silicon [61,62] then increasing sharply upon melting to 0.64 W/cmK as deduced from electrical conductivity measurements [60]. These strong variations must be included in any calculation of the heat flow. Figure 2.1 shows the temperature dependence of the thermal conductivity with the analytical function

$$k(T) = \frac{299}{T-99} \text{ W/cmK} \quad (2.5)$$

Figure 2.1 Thermal conductivity of silicon as a function of temperature. The triangles are experimental values, and the solid curve indicates the fit for the form of conductivity used in the model (ref.61).

obtained by a least-squares fit to experimental data in the solid phase. In the liquid phase a constant thermal conductivity can be used since the temperature usually remains close to the melting point.

2.2.3 Absorption Coefficient

The optical properties of silicon are also affected by the temperature. Since the absorption of light in silicon is an indirect process which requires a series of interactions with lattice vibrations the absorption coefficient increases exponentially with temperature for all photon energies [63]. In the case of an argon ion laser operating in multiline mode (with wavelengths 488 and 514 nm)

$$\alpha = 7.5 \times 10^3 \exp(T/435) \quad (2.6)$$

Since liquid silicon behaves like a metal the absorption coefficient increases to a maximum value of 10^6 cm^{-1} [64].

2.2.4 Reflectivity

The reflectivity increases gradually with temperature, as long

as the silicon is in the solid state, and is usually described by a simple linear function [61]:

$$R(T) = 0.367 + 4.29 \times 10^{-5} T \quad (2.7)$$

The reflectivity change upon melting affects significantly the efficiency of the energy coupling to the solid. Melting begins by the formation of a very thin liquid film at the center of the laser spot. As the depth of this liquid increases thin film optical interference effects cause the reflectivity of the sample to increase continuously with the thickness of the liquid film from the lower solid state value (0.44) to the higher liquid state value (0.72) when the liquid film thickness reaches $0.03 \mu\text{m}$ [64]. This reflectivity variation, can be calculated using classical plane wave optical techniques [65], and is shown in Fig. 2.2 for the case of the argon laser beam.

2.3 Review of Temperature Rise Calculations

The temperature rise in a sample being heated by a source (S) can be calculated using the energy conservation principle which leads to the well known heat flow equation:

Figure 2.2 Reflectivity of a liquid silicon film on a solid silicon substrate at $\lambda = 0.5 \mu\text{m}$ (ref.64).

$$c_p \rho \frac{\partial T}{\partial t} = \text{div} (k \text{ grad } T) + (1-R)S \quad (2.8)$$

In the case of pulsed laser annealing the large beam diameter and very short dwell time allow the use of a simple 1-D heat flow model reducing the complexity of the calculation. Both analytical methods using Green's function technique with a perturbation approach [66,67] and an adiabatic approximation [68], as well as numerical methods based on the finite difference technique [69-72] have been employed to solve the heat diffusion, and in a few cases the energy coupling problem as well.

In the case of cw laser annealing, because of

- (a) the small diameter of the beam that results in a temperature gradient in the lateral direction comparable to that in the direction perpendicular to the surface and
- (b) the relatively long dwell time that allows significant heat diffusion,

the effect of lateral heat diffusion can not be neglected and the use of a 3-D model is necessary. The first calculation for cw laser annealing was carried out by Lax [73,74] and has been subsequently modified to include the effects of elliptic beam and time dependence [75] and phase transition in a restricted way [61]. Lately the model has been extended to include the effect of multilayer structures [76,77]. All these calculations were based on the Green's

function formalism [78] but have been limited to the solid state regime, due to the difficulties involved with solving the nonlinear thermal diffusion equation which results when melting effects are included. The only calculation that included the sharp increase in reflectivity when melting occurs, and so yielded meaningful values for the temperature rise beyond melting along with the thickness of the molten layer, was given by Kokorovsky et al. [64], but even that treatment was restricted to the time independent problem.

During conventional cw laser annealing, which is carried out with scanning speed less than 10cm/s, the sample has sufficient time to reach thermal equilibrium with the heat source so that only the steady state solution is required - the time dependence of the temperature rise is not important. In the present experiment, however, in order to controllably melt a thin silicon layer without creating extensive crystal damage, it is essential to use high scan speed which is above 50 cm/s. It becomes apparent, that under this condition the scanning speed or dwell time has a decisive effect on the temperature rise, indicating that it is a non-steady state process.

To gain insight into the dynamic behavior of the temperature rise during cw laser annealing a computer simulation of the general time dependent heat diffusion equation has been carried out. The model includes temperature dependent thermal and optical material properties and the effects of phase transition when melting occurs. While similar analyses have been carried out for the essentially 1-D

problem of pulsed laser annealing, to our knowledge this is the first time that cw laser annealing has been investigated in such a general manner. The following chapter will describe this novel time dependent computer simulation.

CHAPTER 3

NUMERICAL SIMULATION OF THE HEAT FLOW PROBLEM

In this chapter first a novel formulation of the heat flow problem for cw laser annealing will be presented, which is intended to reduce the amount of computation necessary to solve the 3-D problem. Then the numerical method, developed to solve the strongly nonlinear, parabolic partial differential equation system, will be described. Finally the results of the numerical computation will be presented and discussed.

3.1 Formulation of the Heat Equation

The 3-D heat equation which governs the temperature rise $T(z,r,t)$ due to a heat source S , which is in this case the laser energy absorbed by the solid, expressed in cylindrical coordinates to explore the symmetry of the problem is:

$$\frac{\partial H}{\partial t} = \frac{\partial}{\partial r} \left(k \frac{\partial T}{\partial r} \right) + \frac{k(T)}{r} \frac{\partial T}{\partial r} + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + (1-R(T)) S(z,r,T) \quad (3.1)$$

subject to the usual boundary conditions:

$$\frac{\partial T}{\partial z} = 0 \quad \text{at } z=0, \quad (3.2)$$

$$T(z=d, t) = T_B$$

which are based on the assumption that no heat is lost from the front surface and the back surface stays at constant temperature. H is the heat enthalpy and k is the temperature dependent thermal conductivity.

The coordinate system is set up in such a way that the z axis lies along the center of the laser beam with $z=0$ being at the surface of the material and d is the thickness of the sample (see Fig. 3.1).

The onset of melting and the motion of the liquid solid interface have paramount importance during laser processing. The usual approach to include it in the numerical calculation is the so-called "front tracking" method in which the position of the moving front is determined at each time step. This technique, however, is well suited only for explicit methods which, as it will be shown later, is not efficient for the present problem. In this case, as an alternative, the problem is formulated in such a way that the conditions at the moving boundary are incorporated into a new equation and the problem is solved without explicit reference to the position of the boundary. This formulation is based on the use of a heat enthalpy function H , which represents the total heat energy accumulated in the solid including the latent heat of fusion H_f and

Figure 3.1 Schematic illustration of the laser beam heating a silicon wafer and the cylindrical coordinate system used for the numerical calculation.

determined by a single equation valid over the whole temperature range.

$$H(T) = \int_{T_B}^T c_V(T') \rho(T') dT' + \Theta(T) H_F \quad (3.3)$$

Where $\Theta(T)$ is the unit step function with the following properties:

$$\Theta(T) = 0 \quad \text{if } T < T_M$$

$$\Theta(T) = 1 \quad \text{if } T > T_M$$

T_M is the melting temperature ($T_M = 1690\text{K}$ for silicon), and T_B is the temperature at which the backsurface is held (chosen to be 600K for the present calculation). The heat of fusion is $H_F = 3200 \text{ J/cm}^3$.

For a Gaussian laser beam having a total incident power P and $1/e$ intensity radius w using Lambert's law

$$S(r, z) = \frac{P}{\pi w^2} \exp\left\{-\frac{r^2}{w^2}\right\} \alpha(T) \exp\left\{-\int_0^z \alpha(z') dz'\right\} \quad (3.4)$$

The reflectivity R depends not only on the temperature but also on the melt depth as was discussed earlier.

This calculation is intended to take into account all the available information on the temperature dependence of thermal and optical properties and also to include the effects of phase transition when melting occurs. Because of the strong nonlinearity

of the problem (specially when melting occurs) and the need to calculate the time evolution of the temperature profile, it is necessary to solve the problem numerically. However, to avoid excessive computer use, in terms of storage space and computation time needed for a fully 3-D calculation, the analysis is restricted to the temperature rise along the center of the laser beam ($r=0$) while still including the important effect of lateral heat diffusion. This can be accomplished through calculating the lateral diffusion at $r=0$ during each time step by solving two coupled 1-D differential equations simultaneously.

The first two terms on the right hand side of equation (3.1) describe the lateral diffusion components. It is possible to develop a second equation that can be used to calculate these terms. For small r the radial temperature distribution is approximated by a Gaussian function:

$$T(z,r,t) = T_z(z,t) \exp \left\{ r^2 \frac{L(z,t)}{4T_z} \right\} + T_0 \quad (3.5)$$

T_z is the temperature increase with respect to either $T_0=T_B$ in the solid phase or $T_0=T_M$ in the liquid phase and $kL<0$ is the lateral diffusion at $r=0$. Since the temperature does not change at the liquid-solid interface (r_1), approximation (3.5) can only be used if the temperature increase according to (3.5) is negligible at r_1 , which requires that $r_1^2 |L| / 4T_z \gg 1$. This inequality represents the

assumption that the lateral diffusion at $r=0$ is determined primarily by the local properties of the temperature rise and not affected by the temperature variation elsewhere. Although r_1 is not being calculated here, in the present experiment with $w=20 \mu\text{m}$ r_1 was measured to be greater than $5 \mu\text{m}$. Since the temperature rise is only affected by the lateral heat diffusion if $|L| > 5 \times 10^8 \text{ K/cm}^2$, the validity of the model is limited to small temperature rises and melt depths. This condition was checked during the calculation and resulted in an upper limit for the melt depth of around $1 \mu\text{m}$, which is not a severe restriction in most applications.

If expression (3.5) is substituted into (3.1) and $r=0$, a 1-D equation results for the temperature rise (T_z) along $r=0$, which also contains L . A second equation can be obtained by calculating the second derivative of equation (3.1) according to r using the same substitution and then taking $r=0$. The two coupled differential equations are:

$$\frac{\partial H}{\partial t} = kL + \frac{\partial}{\partial z} \left(k \frac{\partial T_z}{\partial z} \right) + (1-R) S \quad (3.6a)$$

$$\frac{\partial H_L}{\partial t} = -2 \frac{k}{T_z} L^2 + \frac{\partial}{\partial z} \left(k \frac{\partial L}{\partial z} \right) - ((1-R) \frac{4}{w^2} + \frac{\partial R}{\partial T} L) S \quad (3.6b)$$

where $H_L = L(c_v \rho + \delta(T_z - T_M) H_F)$, and δ is the well known delta function obtained from differentiating the unit step function.

By simultaneously solving these two 1-D equations the

temperature rise can be obtained as if it were calculated in a 3-D model. The second differential equation (3.6b) can be used to calculate L . Since this equation depends very little on the small variation of the temperature an approximate solution for T_z can be used here to determine L at each time step, which then can be used to solve (3.6a) to obtain the exact value of the temperature increase.

3.2 Numerical Method

Because of the long time period involved, a numerical method which guarantees convergency even for large time steps has to be selected. The Backward-Euler implicit method [79], which imposes no restriction on the time steps and was found to be efficient in dealing with strongly nonlinear problems was chosen to solve the partial differential equations.

$$\frac{H(T_i(t+h)) - H(T_i(t))}{h} = G(T_{i-1}(t+h), T_i(t+h), T_{i+1}(t+h)) \quad (3.7)$$

$T_i(t)$ is the temperature at the i -th grid point, h is the time step, and G is the right hand side of the equation expressed using finite differences. This method uses the solution being obtained to express the increase during the time step (Fig. 3.2) and consequently requires iteration to carry out the calculation. An explicit method,

Figure 3.2 Schematic representation of the Backward Euler numerical method.

which determines the solution at the advanced time level using only the result obtained at the previous time level, is only convergent if the ratio between the time steps and the square of the grid spacing is less than $1/2$, which requirement in our case would lead to an unacceptably large amount of computation.

An implicit method such as the Backward-Euler formula is always convergent for linear problems independently of the ratio between the time steps and grid spacing. For a nonlinear problem, however, such as the one being dealt with, convergence proofs are lacking for any serious generalization of the heat equation. It is still reasonable to assume that the method is convergent for a particular problem if certain restrictions with respect to the grid spacing and time steps are introduced [80,81]. Experience also shows that this method is very efficient in dealing with strongly nonlinear problems.

During the computation iteration has to be used at each time step to determine the new temperature distribution. (3.7) can be rewritten in the following form:

$$F_i\{T_i(t), T_{i-1}(t+h), T_i(t+h), T_{i+1}(t+h), R(T_i(t+h))\} = 0 \quad (3.8)$$

$$\text{for } i=1, 2, \dots, N$$

The nonlinear equation system which results from this method is solved using Newton's iteration [82] with Gauss's elimination technique [81]. This involves repeatedly solving the following linear equation system:

$$F_i(t) + \sum_{j=1}^N \left. \frac{\partial F_i}{\partial T_j} \right|_{T_j=T_j^*} (T_j(t+h) - T_j^*) = 0 \quad i=1,2,\dots,N \quad (3.9)$$

where $\left. \frac{\partial F_i}{\partial T_j} \right|_{T_j=T_j^*}$ is a $N \times N$ tridiagonal matrix

if $\frac{\partial F_i}{\partial T_j} = 0$ for $j < i-1$ and $j > i+1$

T_j^* is an approximate solution, which is first calculated by using a simple explicit method.

The computer program which was developed to solve partial differential equation system (3.6) by carrying out the calculation outlined above is given in Appendix A.

To represent sharply varying functions (such as $S(z)$) at the surface and still cover the total thickness of the silicon wafer with the minimum number of grid points a nonequidistant grid structure is used. The smallest distance between two grid points is 5×10^{-7} cm at the surface which then increases continuously to extend over 280 μ m using only 92 grid points.

Time steps are optimized at each iteration according to (a) the speed of convergency to minimize the amount of computation necessary to carry out the calculation for a certain length of time, (b) to

maintain adequate representation of fast changing functions in time to ensure the validity of the numerical solution.

During the initial phase of melting the reflectivity increases sharply as it varies with the melt depth resulting in a situation where a simple tridiagonal matrix is not sufficient to represent F_i/T_j which is required for the Newton iteration. In order to avoid using a more complicated matrix a special method is used to ensure convergency. First the reflectivity is taken to be constant during the iteration then a new reflectivity is approximated based on previously calculated values and the error between the assumed and calculated reflectivities using again Newton iteration. This process is repeated until the new reflectivity is determined with sufficient precision.

The melt depth is determined by fitting a fourth order polynomial on the temperatures around the melting point.

Once the new temperature profile is calculated the second partial differential equation is solved using a similar method to calculate the new lateral diffusion which is then used to calculate the temperature profile. Since the variation of the lateral diffusion (L) depends mostly on the time steps and only very little on the temperature one iteration is enough to find the simultaneous solution of the two equations.

For computational purposes, phase transition is modeled by increasing H and k in a temperature range of $2K$ using the following

function:

$$f(T) = 1/(\exp(T-T_M) + 1) \quad (3.10)$$

The validity of the solution in the strongly nonlinear region was tested by comparing numerical results obtained by using different solution techniques and various time steps and grid spacings.

The computation of the temperature rise during the annealing process which involves the melting of a 1 μ m thick layer requires about 10 minutes CPU time on a Honeywell CP6 mainframe computer.

3.3 Results

The calculation was carried out for single crystal silicon being irradiated by a 40 μ m 1/e diameter cw argon laser beam ($\lambda = 0.5 \mu$ m). The temperature dependent specific heat, mass density product and the thermal conductivity were included using analytical functions fitted to experimental data.

The numerical results shown in Fig. 3.3 demonstrate the effect of phase transition on the time evolution of the temperature profile. The surface temperature increases rapidly from the 600K initial value as long as the silicon is in the solid state (region a). When the maximum surface temperature rises above the melting point the

Figure 3.3 Calculated temperature rise at different distances from the surface and melt depth as a function of time during irradiation of a single crystal silicon with 6 W stationary cw laser beam. The reflectivity variation during melting is also shown.

formation of a thin liquid layer, which is accompanied by an increase in reflectivity, results in a sharp decrease in the rate of the temperature rise. During the subsequent time period (region b) the surface temperature stays virtually constant allowing the diffusion of more heat into the bulk. This process eventually leads to the decrease of the temperature gradient in the surface region. As a result a higher portion of the absorbed heat energy will accumulate at the surface leading to a small increase of the temperature along with the increase of the melt depth which causes a further increase in reflectivity (i.e., negative feedback). During this transient period, the increasing loss in absorbed energy is balanced by the decrease in the heat diffusion from the surface. If the incident laser power is above a certain threshold value and sufficient time has elapsed the reflectivity reaches its maximum value and the surface temperature starts rising again at a higher rate (region c), before it reaches the steady state value.

Fig. 3.4 shows the time evolution of the melt depth for different incident laser powers. There exists a threshold in power (approx. 4.8W) under which no melting occurs. For laser powers above but still close to this threshold value the melt depth is a slowly increasing function of the dwell time. From these results it is expected, that for short dwell time the maximum temperature rise and melt depth is determined by the transient behavior rather than the steady state solution of the heat flow problem. Since dwell time can be measured and controlled easier (by adjusting the scanning speed)

Figure 3.4 The propagation of the melt front as a function of time during melting of a single crystal silicon with a stationary cw laser beam at different laser powers.

than the laser power, dwell time can be used to exert better control over the propagation of the melt front.

The calculation can be extended to moving laser beams, if the asymmetry of the lateral diffusion generated by the moving beam is neglected, by changing the laser power according to the Gaussian distribution of the beam. Since melting usually occurs while the surface is heated by the center part of the laser beam this approximation is not expected to introduce significant error.

Figure 3.5 shows the propagation of the melt front along the z axis as the laser beam is scanned across this axis at a speed of 100 cm/s. The center part of the beam reaches this axis at $t=0$. These curves also allow us to estimate the velocity of the solid-liquid interface during recrystallization. For the typical scanning speed of 100 cm/s this solidification rate is between 2-5 cm/s which is more than an order of magnitude slower than in the case of pulsed laser annealing (which is usually over 1 m/s).

Results, shown in Fig. 3.6, demonstrate that the maximum melt depth depends strongly on the scanning speed, and that it becomes less sensitive to the laser power as the scanning speed increases thus improving the reproducibility of the melting process.

As a conclusion of this chapter it can be noted, that:

- (a) For scanning speeds higher than 10 cm/s the heating of a silicon wafer by a cw laser beam becomes a non-steady

Figure 3.5 The time evolution of the melt front during melting of a single crystal silicon with a cw laser beam scanned at 100 cm/s velocity calculated for three different laser powers.

Figure 3.6 Calculated maximum melt depth as a function of laser power for a single crystal silicon irradiated by a cw laser beam scanned at different speeds.

state process, which can only be analyzed by solving the time dependent heat flow equation.

- (b) The maximum temperature rise and melt depth are not only functions of the laser power but depend also on the scanning speed (or dwell time) as well.
- (c) At high scanning speed the maximum melt depth is less sensitive to the laser power improving the reproducibility of the melting process.

CHAPTER 4

EXPERIMENTAL CONSIDERATIONS AND CONDITIONS

As was briefly outlined in Chapter 1. both pulsed and cw laser processing require careful considerations to minimize damage introduced during processing. It was also pointed out that in order to induce diffusion it is necessary to melt a thin surface layer of the silicon. While in the past this process almost exclusively employed pulsed lasers; in the present work a new approach, which employs a cw laser with high scanning speed, was chosen.

It has already been shown, based on the numerical simulation of the heat flow during laser-induced melting, that high speed scanning of the laser beam offers the possibility of well controlled melting of a thin layer and improved reproducibility due to the decreased sensitivity on the laser power. There are, however, various other processes involved in cw laser-induced liquid phase diffusion (beside the heat flow) which are difficult to model, yet have to be considered to find the optimum processing condition.

In this chapter first the various considerations concerning the origin of laser induced damage and techniques to minimize them will be discussed. After that a novel high speed laser beam scanner system, required to provide optimum conditions during laser

processing, will be presented, and finally the special role of the phosphosilicate glass diffusion source will be described.

4.1 The Origin of Laser-Induced Damage

Although there is universal acceptance of the fact that ion implanted layers can be laser annealed to a state of high electrical activity of the implanted dopant and complete absence of macroscopic defects such as dislocations, stacking faults and precipitates; laser processing can also introduce defects which can severely deteriorate the electrical characteristics of semiconductor devices [83-85]. For a particular application it is always necessary to find the optimum condition under which undesirable effects are minimized.

The following general observations may be drawn from the numerous experimental investigations of electronic defects in cw laser processed single crystal silicon:

a/ Stress gradients:

One of the origins of laser-induced crystal defects is the stress gradients created by high temperature differences. Liquid phase processing which involves short times and very high gradients does not, typically, yield misfit arrays of dislocations. However, in the solid phase regime, gradients extend deeper for longer times and

substrate heating is often required to avoid dislocation generation [86]. For that reason samples are kept at 600K during laser processing. Since cw laser annealing allows a longer time for heat diffusion and consequently results in lower temperature gradients than pulsed laser annealing the problem of dislocation generation, connected to the presence of the liquid phase, is expected to be less severe in this case.

b/ Crystal growth:

The very rapid interface velocities characteristic of liquid phase processing may produce defect trapping during epitaxial regrowth. The rate of epitaxy is controlled by the interface temperature gradient (evolution of heat of fusion) and atomic motion in the liquid. At high interface velocities, nonequilibrium defects may be trapped due to their low mobility in the solid state. Again since cw laser annealing results in a liquid solid interface motion about an order of magnitude slower than pulsed laser annealing (see Fig. 3.5) a better quality epitaxial layer is expected.

c/ Surface contamination:

Since any contamination on the surface diffuses together with the dopant it is important to protect the surface during processing. The phosphosilicate glass which is deposited after the wafers have been thoroughly cleaned - primarily to serve as a diffusion source, also acts as a protective layer so that laser processing can be

carried out in an air ambient.

d/ Point defects:

Even in the absence of extended crystallographic defects in the annealed layer it has been demonstrated, using Deep Level Transient Spectroscopy [87] and defect luminescence measurement [88], that laser annealing induces residual electrically active point defects. In a study of the influence of scan speed on deep level defects it has been found that the average defect concentration decreases by almost two orders of magnitude as the scan speed is increased from 1-100 cm/s for a fixed temperature distribution in the material [89]. Low temperature (450-800 C) furnace annealing after laser processing has been found effective to remove point defects. In the present experiment an 800C 10 minutes H₂ furnace annealing is included following laser processing.

e/ Si-SiO₂ interface:

When laser annealing takes place through a SiO₂ layer the removal of dislocations as a result of melting has been proven [84]. However, it is important not to exceed the melting point of the SiO₂ (melting point of Si=1690 K, of SiO₂=1970 K) since the dissolved oxygen leads to the formation of stacking faults and other defects. The numerical computation showed that during melting of a thin surface layer (1 μm) the temperature rise is very slow and limited to less than 50-100 K above the melting point of silicon.

f/ Liquid flow:

Another danger associated with melting of silicon is the possibility of liquid flow of the molten layer due to surface-tension gradients. At the center of the molten pool of liquid, the temperature of the liquid is highest and the surface tension is at its lowest value. The increase in surface tension away from the beam axis results in a movement of liquid away from the center, which depresses the surface of the liquid under the beam and raises the liquid surface at the periphery of the liquid region [90]. This can result in an uneven surface, the generation of misfit dislocations and poor Si-SiO₂ interface quality.

Since the aim of this work is to induce liquid phase diffusion using a cw laser, which process involves substantially longer dwell time than pulsed laser annealing, extreme care has to be taken to avoid defect generation due to the presence of molten silicon.

4.2 High Speed Scanning of the Laser Beam

The problem of liquid flow can be circumvented by scanning the laser beam at a relatively high speed. Though this possibility has already been suggested in a different context [91], to the author's knowledge, this technique has not yet been applied in the area of laser-induced diffusion. Detailed calculation indicates [91] that

above a threshold scanning velocity, surface rippling can be suppressed by decreased dwell time so that no significant displacement of liquid can take place.

Fast scanning of the laser beam, as was mentioned earlier, also decreases the defect concentration generated by the annealing process. It has also been shown that this technique is advantageous in other laser processing applications such as thermal etching or recrystallization [92]. Furthermore it also increases the throughput of the process.

To realize this experimental condition, an optical laser beam scanner was designed and built.

Every laser scanning system combines a variety of optical mechanical and electronic components to achieve a particular goal. There are basically two techniques of annealing a large area by a laser beam focused to a small spot size: (a) moving the sample being annealed by means of a translating x-y stage while the beam is kept stationary, or (b) by scanning the beam by means of a vibrating mirror. In the first case the position can be controlled very precisely and the spot size is not affected by the scanning, however, due to the necessity of moving a large mass the scanning speed is limited to less than 10 cm/s. The second approach allows high scanning speed but makes it difficult to maintain high spatial resolution required to control the distance between two adjacent scans.

Based on these considerations a new approach was adopted which employs both basic techniques. The scanning system designed combines the high speed of a vibrating mirror that can scan the beam up to 500 cm/s in the x direction with the precision of a stepping motor driven translating stage, which moves the beam in the y direction at low speed (<2 cm/s) between two scans. The two motions are coupled by placing the optical part of the system on the translating stage. In this arrangement the sample holder is stationary which allows greater flexibility in controlling the environment of the sample. Figure 4.1 shows the laser annealing setup, including the beam scanner and the sample holder.

4.2.1 Optical Considerations

The important property of a Gaussian laser beam is that it can be focused into an extremely small spot with extremely high energy density. The spot size is limited by the basic optical diffraction. The collimated laser beam is simply a particularly long Gaussian beam waist (see Fig 4.2). The spot size $w(z)$ of the laser beam as a function of distance from the waist and the minimum spot size w_0 are given [93] as:

Figure 4.1 Photograph of the high speed laser beam scanner which includes a vibrating mirror placed on a translating stage.

Figure 4.2 Schematic illustration of the collimated Gaussian laser beam.

$$w(z) = w_0 \left\{ 1 + \left(\frac{\lambda z}{w_0^2} \right)^2 \right\}^{1/2} \quad (4.1 a)$$

$$w_0 = \frac{\sqrt{2} f \lambda}{\pi d_b} \quad (4.1 b)$$

Where d_b is the $1/e$ diameter of the laser beam prior to focusing and f is the focal length of the focusing lens. Unfortunately, there is an inverse trade-off between the spot size at which the beam is collimated and the distance over which the beam will remain collimated.

As the beam is swept across the sample by tilting the mirror, the distance the light travels between the focusing lens and the sample, varies resulting in a slightly changing beam diameter and energy density. If the use of a very expensive flat field lens system which corrects for this error is to be avoided a lens with a long enough focal length should be used.

The scanning system was designed in such a way that focusing lenses up to 350 mm focal length can be installed to provide for a relatively long range around the focal point, within which the same energy density can be maintained along the whole scanned line.

The laser used is a Coherent CR-18 SG cw argon ion laser which has a maximum output power of 18 W when operating at all lines (including wavelengths between 458-515 nm) in TM₀₀ mode. The $1/e$ diameter of the Gaussian beam is 1.8 mm [94].

During the experiments the laser beam was focused by a 160 mm lens leading to a diffraction limited spot size of 40 μ m diameter. This guarantees an energy density variation of less than 2% within a 3 cm long scan.

4.2.2 Laser Beam Scanner

The block diagram of the control and monitoring units of the scanning system is shown in Figure 4.3.

The scanning process is controlled by a microprocessor based microcomputer (KIM-1 board from MOS Technology Inc.). The controller is connected to the driver of the stepping motor and the scanning control amplifier. The optical scanner is a moving iron galvanometer with a position transducer designed for closed-loop operation. The scanner control includes an adjustable-frequency sawtooth generator and a temperature control amplifier to maintain scanner temperature regulation to better than 0.5 degree C.

The position of the mirror and the reflected light intensity which is monitored by a photovoltaic cell are displayed on an oscilloscope. For precise measurement of the scan time a counter is used. The program of the microcomputer is stored on an audio tape.

The rotation of the vibrating mirror and the motion of the

Figure 4.3 Block diagram of the beam scanner control units.

translating stage are synchronized in such a way that, after each scan performed in the x direction by tilting the mirror, the translating stage moves the selected distance in the y direction. The next scan only starts after this motion is completed followed by a predetermined delay period during which mechanical vibrations settle. By repeating this sequence the laser beam can be scanned over a selected area of the wafer if necessary several times.

The detailed timing diagrams of the control signals are shown in Figure 444. At the beginning of a scan cycle (time instant A) the controller sends out an enable signal to the scanner control amplifier which starts a ramp signal that controls the deflection of the mirror. The ramp amplitude (angular rotation of the mirror) and the rise time (scan time) can be set by the front panel controls of the amplifier. When the scan is finished (B) the scanner driver sends out a synchronization signal (40 μ s 15 V) corresponding to the retrace interval of the ramp. After receiving this signal the controller allows 3 ms for the mirror to return to its original position and then sends out a step signal to the driver of the stepping motor (C). This is followed by a 25 ms delay after which a new enable signal is generated (A) to start the next scan cycle. After a certain "number of scans" determined by the content of memory (15) the scanning either stops or is repeated moving to the opposite direction depending on the "number of repetitions" stored in memory (20).

The width of the scanned area (number of scans) and the number of repetitions is controlled through the program of the microcomputer

Figure 4.4 Timing diagrams of the beam scanner control signals.

The listing of the assembly language code for the 6502 microprocessor is given in Appendix B.

The scanning velocity of the beam and the length of one scan can be set through the controller of the optical scanner. The duration of a scan can be set between 2 s and 3 ms. The maximum length of the scan depends on the focusing lens used. The excursion range of the scanner is up to 25 degrees of mirror rotation. The minimum movement of the translating stage is one step which is 6 μm .

4.2.3 Sample Holder

The sample holder provides for heating of the sample and the possibility of controlling its environment.

The sample is held on to a brass block by a vacuum chuck. Uniform heating of the sample is achieved by heating the brass block by resistance heater and monitoring the temperature through a temperature sensitive resistance which is connected to a temperature controller. The sample temperature can be set from room temperature to 350 C.

The brass block is enclosed in a stainless steel, vacuum tight, chamber. The laser beam is coupled to the sample through a quartz window.

The chamber is provided with an inlet and an outlet to allow any gaseous environment for the sample. This, however, is only important if laser annealing is carried out without any encapsulation such as the phosphosilicate glass or a chemical reaction is to be induced in the gas phase.

The whole sample holder is mounted on a micrometer driven stage that allows precise vertical movement in order to adjust the distance between the lens and the sample.

4.3 Phosphosilicate Glass

Phosphosilicate glass (PSG) was chosen as diffusion source for phosphorus diffusion, based on the following considerations. PSG can be formed at low temperatures (300-500 C) by chemical vapor deposition (CVD) and has been widely used in the fabrication of semiconductor devices, for such purposes as the stabilization of electrical characteristics, insulation of multilayer interconnection, and scratch protection.

The formation on heated substrates of vitreous SiO_2 films by reacting dilute SiH_4 with excess O_2 proceeds by a complex heterogeneous mechanism that involves surface adsorption and catalysis leading progressively to SiO_2 as the solid end product. Cooxidation of diluted PH_3 with SiH_4 plus excess O_2 at 300-500 C

leads to phosphosilicate glasses, $(\text{SiO}_2)_{1-x}(\text{P}_2\text{O}_5)_x$. The quality of the glass, the deposition rate and the mole % of P_2O_5 can be affected by substrate temperature, O_2 /hydride ratio, SiH_4/PH_3 ratio, and flow rates. Usually the plateau region is selected where the rate of growth is maximum for a given temperature, and is insensitive to the O_2/SiH_4 ratio. The composition of PSG films can be varied by varying the $\text{PH}_3/\text{SiH}_4+\text{PH}_3$ ratio but also affected by the O_2/SiH_4 ratio [95] (see Fig. 4.5).

4.3.1 Antireflective Coat

The silica glass film is intended to protect and improve the stability of the silicon surface during laser annealing. The other important advantage of using such a layer is that it can act as an antireflective coat if the proper thickness is selected.

Figure 4.6 illustrates the propagation of a laser beam through a glass film covering a single crystal silicon substrate. The optical properties of air, SiO_2 , and Si are described by the refractive indices n_1, n_2, n_3 respectively. Since the amplitude of the electromagnetic field decreases due to absorption (discussed in Chapter 2) the propagation of light in silicon is described by a complex refractive index. The total reflected light is the sum of the

Figure 4.5 (a) Deposition rate of PSG films as a function of $O_2/(SiH_4+PH_3)$ ratio and substrate temperature. $SiH_4/PH_3=14.1$ (ref. 95) (b) Composition of PSG films in wt.% and in mole % P_2O_5 as a function of $O_2/(SiH_4+PH_3)$ ratio (ref. 95) (c) Mole % of P_2O_5 in the PSG films vs. $PH_3/(SiH_4+PH_3)$ ratio (ref. 96).

Figure 4.6 Reflection of the laser beam from an air/SiO₂/Si system.

reflected beams from the two interfaces and at normal incidence can be calculated as a function of the thickness of the antireflective coat by the following equation [65]:

$$R = \left(\frac{r_{12} + r_{23} \exp(4\pi n_2 d_0 / \lambda)}{1 + r_{12} r_{23} \exp(4\pi n_2 d_0 / \lambda)} \right)^2 \quad (4.2)$$

$$\text{where } r_{12} = \frac{n_1 - n_2}{n_1 + n_2} \quad r_{23} = \frac{n_2 - n_3}{n_2 + n_3}$$

Figure 4.7 shows the dependence of the reflectivity on the thickness of the oxide layer computed using (4.2) for both solid and liquid silicon substrates. The refractive indices used were $n_1=1$ for air, $n_2=1.46$ for SiO_2 , and $n_3=4.69-i0.093$ for solid and $n_3=2.2-i4.5$ for liquid silicon. The reflectivity exhibits a periodic change as a function of the PSG thickness. The minimum reflectivity occurs at approximately 86, 260, 428, etc. nm. For ease of controllability the thickness 260 nm was selected for the present experiment.

As a result of this, the laser annealing process becomes selective, since the silicon surface coated with the suitable thickness of glass layer will absorb more of the incident laser energy than the rest of the wafer which is coated with an additional oxide layer and reflect a higher proportion of the beam energy.

Figure 4.7 Reflectivity of the SiO_2 coated Si substrate as a function of oxide thickness, for solid and molten silicon at $\lambda = 0.5 \mu\text{m}$.

4.3.2 Phosphosilicate Glass as Diffusion Source

The doped oxide diffusion system is different from other sources such as, gaseous, liquid or thin film of the dopant material, in two basic aspects. First, because the oxide phase has much lower dopant diffusivities than silicon (see Figure 4.8) it imposes serious constraints on the availability of diffusing substance for the substrate and, second, there is a chemical transformation of the diffusing species at the oxide-silicon interface. Consequently the P concentration in the silicon will be lower than that achieved by the conventional high temperature gaseous diffusion process.

If this becomes critical an additional deposition of the desired dopant material by evaporation in vacuum, prior to the silica glass deposition, can be included. This, however, does not affect the role of the glass layer during laser annealing. Also this method can be employed to extend the application of this technique for the diffusion of several other dopants.

The phosphorus content of the silica glass is expected to be in the order of 10-20 mole % of P_2O_5 , which is equivalent to $1-2 \times 10^{21} \text{ cm}^{-3}$ P concentration, as estimated from the deposition condition using experimentally determined relationships between the mole % of the PH_3 in the gas mixture ($SiH_4 + PH_3$) during deposition and the P_2O_5 content of the glass layer.

During a typical conventional furnace diffusion the doped oxide

Figure 4.8 Arrhenius plot of the phosphorus diffusivity in silicon and in doped deposited oxide (ref. 98).

behaves like a constant level reservoir of dopant [97]. The diffusion process is determined by the diffusivity of phosphorus in both the oxide and silicon and also by the physico-chemical processes at the interface as P_2O_5 converts into elemental form at the interface by reacting with silicon.

The diffusivity of P in the oxide and the reaction rates of the forward and backward reactions, the ratio of which in equilibrium is often referred to as segregation coefficient, were determined at moderate temperatures [98,99].

Under the extreme conditions of laser-induced liquid phase diffusion, the details of these processes have not yet been studied. The classical diffusion theory, using constant diffusivity and neglecting the effect of chemical reactions, predicts that the dopant in the silicon-dioxide is depleted according to an erf function:

$$C_{OX}(t) = C_{OX}^0 \operatorname{erf}\left(\frac{|x|}{2(D_{OX} t)^{1/2}}\right) \quad (4.3)$$

C_{OX}^0 and $C_{OX}(t)$ are the phosphorus concentration in the silicon-dioxide at the beginning of the process and after time t has elapsed respectively, D_{OX} is the constant diffusivity of phosphorus in the silicon-dioxide. Using the diffusivity value of $5 \times 10^{-13} \text{ cm}^2/\text{s}$ at the melting temperature of silicon, extrapolated from data obtained at

lower temperatures [98], the phosphosilicate glass would only be depleted within less than 1 angstrom after a dwell time of 100 s according to formula (4.3). Within such a short distance the concept of diffusion is clearly not applicable.

Significant deviations from the classical diffusion model can be expected in the case of laser-induced liquid phase diffusion due to the following reasons:

Firstly, the thin layer in the phosphosilicate glass close to the interface where the phosphorus transport takes place is expected to have significantly different physical and chemical properties than in the bulk. The reason for that is the vicinity of the interface, the structural changes that take place at high temperature, which is evident from the decreased etching rate, and the presence of mechanical stresses during laser processing.

Secondly, chemical reactions between the solid phosphosilicate glass and the liquid silicon which eventually determines the dopant flux should be different from the usual solid solid reaction and also likely to be a nonequilibrium process about which no information is available.

Thirdly, since the diffusivity in the liquid silicon (which is approximately $10^{-4} \text{ cm}^2/\text{s}$) is several order of magnitude higher than in the solid phase all the phosphorus entering into the silicon diffuses only in the molten layer. Because the diffusion length $\sqrt{D_L t}$

(0.1 μm for 1 μs) is longer than the melt depth it is expected that the phosphorus concentration decreases only slightly within the molten region and results in a sharp impurity gradient at the solid liquid interface. Consequently the junction depth will coincide with the maximum melt depth achieved during the annealing process (Fig. 4.9).

Because of these difficulties of modeling the processes involved in the laser-induced diffusion, no attempt was made to calculate the concentration or the exact shape of the diffusion profile.

Figure 4.9 Expected phosphorus profile after laser-induced liquid phase diffusion from a phosphosilicate glass source.

CHAPTER 5

EXPERIMENTAL PROCEDURE

In order to test this novel diffusion technique p-n junction diodes were fabricated using the laser-induced diffusion process. The p-n junction is the basic building block of every semiconductor device and can also be used as a test vehicle to characterize the process used for its fabrication. This chapter describes the processing sequence developed to form p-n junction diodes using the cw laser-induced diffusion technique.

First the deposition of the diffusion source followed by the laser processing will be described, then the formation of a reliable contact to the shallow diffusion, based on the use of tungsten silicide, will be discussed. The complete process sequence is shown in Fig. 5.1, while the detailed fabrication schedule is given in Appendix C.

5.1 Deposition of the PSG Diffusion Source

All the silicon wafers used in this experiment were p-type (100) orientation with resistivity between 1.6-2.2 ohm-cm. The fabrication

Figure 5.1 Sequence of processing steps used to form p-n junctions: (a) deposition of PSG, (b) cw laser processing, (c) tungsten silicide and (d) Al contact formation.

process starts with a standard prefurnace cleaning procedure which removes the organic contaminants and heavy metals. After this a thermal oxide of approx. $1\text{ }\mu\text{m}$ thick is grown on the surface by wet oxidation. The area of the diode is defined by opening windows into this oxide layer using photolithographic processes. Additional wafers, which were used only to measure the junction depth, had all the oxide removed so that the diffusions were formed on the whole surface of the wafers.

Following this the PSG diffusion source is deposited at $350\text{ }^{\circ}\text{C}$ using the chemical vapor deposition technique described in section 4.3. The gas flow rates of the various components are chosen in such a way that the $\text{O}_2/\text{SiH}_4+\text{PH}_3$ ratio is 5 which ensures that the reaction takes place in the plateau region where the deposition rate is the maximum for a given temperature and the least sensitive to small fluctuations.

First the exact deposition rate was determined for the given temperature and gas flows. The thickness was visually monitored during the deposition by observing the interference colour of the layer and was finally measured by the ellipsometry technique. In practice it was possible to deposit a 260 nm thick layer, required to achieve an AR effect, during a $3\text{ min. }40\text{ sec.}$ long deposition process with a thickness variation of less than 10 nm across the wafer. The phosphorus content of the glass depends on the $\text{PH}_3/\text{SiH}_4+\text{PH}_3$ ratio during deposition. In the present experiment this ratio was around 20% yielding a 10-15 mole % of P_2O_5 in the PSG layer. A higher

concentration of P_2O_5 reacts slowly with atmospheric moisture forming acid products.

5.2 Laser Processing

Laser processing was carried out by raster scanning the cw argon ion laser beam - focused to a spot size of $40\text{ }\mu\text{m}$ - over the whole surface of the wafer using the beam scanner described in section 4.2.2. The spacing between adjacent scan lines was $6\text{ }\mu\text{m}$ so that complete coverage of the surface by the laser beam was ensured. To reduce the thermal stress created by the incident beam at the surface of the wafer, and also to lower the laser power required to melt the silicon, the wafer was held at 600 K (330 C) during the irradiation.

A series of laser processing conditions were tried by varying the laser power and scanning speed. First the optical parts including the mirrors and the focusing lens were aligned at a low laser power. Following this the melting threshold - the laser power required to melt a thin surface layer of the silicon - was determined for the given scanning speed by monitoring the reflected light intensity using a photovoltaic cell. Figure 5.2 shows the experimentally determined melting threshold power. The onset of melting is accompanied with a sharp increase of the reflected light due to the higher reflectivity of the liquid silicon.

Figure 5.2 Measured melting threshold laser power for different scanning speeds, determined from the reflectivity change upon melting.

Laser processing with incident laser power above the melting threshold always results in the formation of a thin diffused layer. The existence of this n-type layer was verified by both a staining technique and electrical measurements which will be discussed in the next chapter. To find the optimum laser processing condition further adjustments of the laser power were carried out after repeated inspections of the change in the appearance of the silicon surface which served as a quick indication of surface melting and damage, and also following the more elaborate junction depth and electrical measurements.

Photographs shown in Fig. 5.3 demonstrate the dramatic difference between the appearance of the silicon surfaces after melting was carried out with a laser beam scanned at 10 cm/s and 100 cm/s velocities. At low scanning speed deep grooves are created as a result of the liquid flow. At higher scanning speed the liquid flow is suppressed and the surface appears to remain smooth in agreement with the theoretical prediction.

These photographs also show the effect of the AR coat. Outside the diode window, where the surface is covered with the thick oxide under the PSG layer, the silicon remained unaffected.

a

b

Figure 5.3 Surface morphology of the silicon wafer after melting it with a laser beam scanned at (a) 10 cm/s and (b) 100 cm/s, at power levels close to the melting threshold values.

5.3 Contact Formation

After laser processing, the PSC layer was removed using Siloxide etch and a new undoped glass layer of 500 nm thick was deposited to protect the surface. It was observed that the etching time for the annealed glass was about twice as long as for the unannealed one implying that the glass layer was densified as a result of the laser processing.

Following this another photolithographic process was used to define the contact areas of the diodes by opening windows into the glass layer.

5.3.1 Tungsten Silicide Formation

To form reliable contacts to the shallow junctions the danger of "spiking" failure, which is the result of the interdiffusion of Si and Al during sintering, has to be overcome [100]. The application of a thin intermediate silicide layer between the silicon substrate and the aluminum contact, which acts as a barrier against diffusion, offers a solution to this problem. Silicides have attracted attention because of their low and metal like resistivity and their compatibility to VLSI technology [101,102].

Silicides can be formed by sintering a thin metal-silicon

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composite deposited by either sputtering, evaporation or CVD techniques [95]. The reaction results in the formation of a clean silicon-silicide interface, with Schottky barriers of reproducible height that can form ohmic contact to appropriately doped silicon.

There are a wide variety of metals that can be used to form silicides, including noble and refractory metals. Both types of silicides could be equally useful as contacts based on their resistivity and Schottky barrier heights, however, only refractory metal silicides possess high temperature stability [104]. Since tungsten silicide has been used in the VLSI environment it was selected for contact formation in the present experiments.

Tungsten can be deposited by e-beam vacuum deposition, sputtering and CVD techniques [95,103]. It has been reported that uniform WSi_2 can be formed by cw laser annealing, but the resultant structure has not yet been studied in any detail or applied in device fabrication [25]. To avoid the uncertainties related to laser-induced silicide formation, in this experiment the standard furnace annealing technique was used to form tungsten silicide. It is worth pointing out, however, that if tungsten silicide is formed also by laser processing all the high temperature furnace annealings are eliminated from the fabrication process.

Tungsten reacts with silicon above 650 C but the reaction rate is strongly affected by the presence of an oxide layer at the interface [100,105], (Fig. 5.4).

Figure 5.4 Tungsten silicide formation (ref.105). Reaction rates for furnace annealing of tungsten deposited (a) with sputter cleaning, (b) without sputter cleaning of the surface oxide. (c) Schematic representation of the model for barrier controlled reaction due to the presence of oxide layer.

A thin tungsten layer of approx. 25 nm was deposited by the RF sputtering technique in argon gas using a pure tungsten target. The thickness of the deposited layer was determined by measuring the tungsten step after longer depositions using an electromechanical transducer which measures the mechanical movement of a stylus as it traverses a film-substrate step. Figure 5.5 shows the result of this measurement which can be used to determine the sputtering time necessary to form a given thickness of tungsten. To ensure an oxide free interface the silicon surface was sputter etched prior to the deposition of the tungsten. The silicide formation was carried out at 800°C in H₂ gas for 10 minutes.

This heat treatment also served as an annealing of the point defects created by the laser processing as was discussed in section 4.1. The temperature and time, however, are not high enough to result any redistribution of the dopants during this annealing process.

To confirm the formation of tungsten silicide the samples were analysed at the Department of Chemistry of the National Research Council of Canada using AUGER spectroscopy combined with sputtering that can yield the depth profile of the ratio of different materials. A typical result is shown in Fig. 5.6. The sputtering rate during the measurement was 2 nm/min. The existence of a layer with constant 2:1 Si to W ratio indicates the formation of the WSi₂. The thickness of the WSi₂ layer is approx. 40 nm. This result also shows that 10 minutes was enough to convert all W into silicide.

Figure 5.5 Tungsten thickness as a function of deposition time for tungsten sputtering with 100 W and 8 mtorr Ar pressure.

Figure 5.6 Depth profiles of tungsten (W), silicon (Si), and oxygen (O) atomic concentration ratios (a) after the deposition of tungsten on the silicon substrate (b) followed by a furnace annealing, as measured by Auger technique combined with sputtering (2 nm/min).

Since the tungsten does not react with the SiO_2 layer it can be removed selectively in Caro's acid without affecting the formed silicide layer.

5.3.2 Aluminum Deposition

The last step in the process was the deposition of the Al contact in vacuum using e-beam evaporation techniques. The layer was patterned by the photolithographic process. The Al showed excellent adhesion to the WSi_2 layer. Finally the back contact was formed using Al and followed by sintering at 450 C in forming gas, to form good ohmic contacts.

CHAPTER 6

CHARACTERIZATION OF THE JUNCTION FORMED
BY LASER-INDUCED DIFFUSION

The diodes formed by the laser-induced diffusion process described in the previous chapter were characterized using techniques based mainly on electrical measurements. These techniques provide the simplest and fastest means to characterize a p-n junction and also directly indicate whether the process is suitable for device fabrication.

Although attempts were made to use the Secondary Ion Mass Spectroscopy (SIMS) technique to determine the distribution of phosphorus in the silicon, it was only possible to detect the existence of phosphorus inside the silicon. Precise profile measurement was made impossible because of the high level of noise at the P line in the particular system used. Other elaborate techniques such as Rutherford Backscattering (RBS) Transmission Electron Microscopy (TEM) and X-ray diffraction etc. can provide more detailed information on the material properties, dopant distribution and crystal defects but require excessive instrumentation and therefore were considered to be beyond the scope of the present investigation.

In this chapter results will first be presented which prove the formation of a n-type layer after laser processing. Following this the quality of the p-n junction will be investigated based on the diode characteristics and finally a capacitance measurement will be used to provide information on the structure of the junction.

6.1 Sheet Resistance

To confirm the existence of a laser-induced diffused layer the current-voltage characteristics of the laser processed regions were first measured. Prior to laser processing n-type contact regions were diffused into the substrate by standard furnace diffusion technique. The laser-processed region was then formed between two such contacts as shown in Fig. 6.1. By applying a suitable voltage between contacts without laser processing or when the laser power was under the melting threshold only a reverse p-n diode characteristic was found. (See Fig. 6.2 a.) Above this threshold laser power the I-V curve turned into an ohmic characteristic (Fig. 6.2 b), indicating that a n-type diffused layer was formed between the contacts as a result of the laser processing.

Once the existence of a n-type layer was proved more precise sheet resistance measurements were carried out using the van der Pauw technique with contacts formed as described in chapter 5. Although

Figure 6.1 Structure used to measure the I-V characteristics of laser processed layers separately from the bulk silicon.

Figure 6.2 I-V characteristics measured between two "contact" diffusions (a) without laser processing or processing with laser power under the melting threshold (the reverse current was enhanced by shining light at the surface of the wafer) (b) after laser processing with sufficient laser power.

sheet resistances as low as 100-200 ohm/ $\square$ were measured for relatively low scanning speed these diffusions showed poor diode characteristics. For the optimum laser processing condition, which required a high scanning speed (100 cm/s), the sheet resistance was found to be in the range of 1000-2000 ohm/ $\square$. These high values can be explained by the limited supply of phosphorus from the glass source, due to its low solid phase diffusivity and interface property. From this result it follows that the dopant concentration is primarily limited by the type of source used, and the lower sheet resistance can only be achieved by using a different diffusion source.

6.2 Junction Depth

Although the concentration profile of the junction was not determined the junction depth was measured using the beveling and staining technique. This method involves the lapping of the junction at a small angle, ϕ , to the surface to enlarge the apparent vertical dimension by a factor of $1/\sin\phi$. Contrast between the n- and p-doped layers is provided by a selective chemical stain. In the present experiment ball beveling was used with 1% copper sulfate and a few drops of concentrated hydrofluoric acid as the staining solution. The action of the stain is to darken the p-type region while leaving the n-type region essentially unchanged.

Fig. 6.3 shows an unpatterned laser-induced diffused layer after

Figure 6.3 Photograph of a laser-induced p-n junction, which was made visible by beveling and staining technique. The lighter colour corresponds to the n-type region.

ball beveling and staining. There is a separate scan line in the middle of the photograph which clearly shows the gaussian profile of the laser beam. The junction depth can be calculated from the radius of the ball and the measured width of the stained region. Using this technique a series of junction depth measurements were carried out for different laser processing conditions. Figure 6.4 compares the measured junction depth to the calculated melt depth for different laser powers and scanning speeds. To minimize the uncertainty inherent in this junction depth measurement technique only diffusions with the same junction depth (around $0.3 \mu\text{m}$) were included. The power values represent the incident laser power required without AR coating in order to be comparable with the calculated results. The ~~AR~~ effect reduces the actual laser power required by approx. 30%.

Although there is an uncertainty associated with determining the exact incident laser power density due to the difficulties involved in the laser power measurement, the estimation of energy loss in the optical system and finally the determination of the spot size at the silicon surface, these errors only affect the absolute value and still allow an adequate measurement of the relative dependence of the melt depth on the laser power and scan speed. It can be concluded that these results show good agreement between the calculated and measured dependence of the melt depth on the laser processing parameters.

Figure 6.4 Calculated laser power required to melt a single crystal silicon at a depth of $0.3 \mu\text{m}$ as a function of the scanning speed, compared with experimentally determined range of laser powers required to induce liquid phase diffusion at a depth of $0.3 \pm 0.1 \mu\text{m}$ for a set of scanning speeds.

6.3 Diode Characteristics

The electrical characteristics of the diode indicate the quality and also the type of the junction formed. Initial measurements were done using a simple curve tracer to study the main features (such as forward bias characteristics, reverse breakdown and to some extent leakage currents) of the diodes.

Figure 6.5 shows typical junction characteristics obtained for various laser processing conditions. For laser powers under the melting threshold no diffusion takes place and the junctions show Schottky diode type characteristics with small forward voltage and "soft" reverse breakdown (Fig. 6.5 a. and d.).

As the laser power was increased the forward bias characteristic of the diode shifted slightly as shown in Fig. 6.5 b, while the reverse characteristic remained virtually the same suggesting that the junction formed was still a Schottky diode with a modified built in potential. This can be explained by the formation of very shallow, probably isolated, diffused regions which can alter the barrier height at the interface [106]. The reverse characteristics of these diodes were soft with breakdown voltages around 10 V.

When the laser power was further increased it resulted in a significant change in the diode characteristics, which are shown in Fig. 6.5 c. and e. These diodes show good p-n junction characteris-

Figure 6.5 Typical measured forward and reverse characteristics of diodes formed by cw laser processing at laser powers (a) (d) smaller than required to melt the silicon, (b) (d) sufficient to cause melting but less than the optimum value, (c) (e) of optimum value.

tics with sharp breakdown over 35 V. This is demonstrated, also by Fig. 6.6 which compares the forward and reverse breakdown characteristics of diodes formed by laser-induced and standard furnace diffusions. This result is explained by the formation of a continuous diffused layer with thickness between 0.2-0.4 μm , according to the junction depth measurement. The range of laser powers where good p-n junctions were formed - and which represents the optimum laser processing condition - is very narrow, typically, around 7.5 W.

For laser powers above this optimum value the junction characteristics rapidly deteriorate exhibiting very high leakage currents which suggests the presence of extensive crystal damage introduced by the laser processing.

More accurate forward and reverse I-V curves, measured by an electrometer, are shown in Fig. 6.7 and 6.8. These plots represent typical characteristics of diodes formed under the optimum laser processing condition. The forward current follows the diode equation:

$$J = J_s \exp(qV/nkT-1) \quad (6.1)$$

Here q , V , k and T are electron charge, voltage, Boltzmann's constant and temperature respectively and where the value n depends on the dominating conduction mechanism. The saturation current J_s is 6×10^{-7} A/cm^2 . The diode quality factor n is 1.7 suggesting a relatively high density of generation-recombination centers. The reverse leakage current is around 10^{-6} - 10^{-5} A/cm^2 for small reverse bias. This

Figure 6.6 Forward and reverse characteristics of diodes formed by (a) the furnace diffusion and (b) the laser-induced diffusion.

Figure 6.7 Log I-V characteristics of a junction formed by the cw laser-induced diffusion.

Figure 6.8 Reverse leakage current characteristic of diode formed by the cw laser-induced diffusion.

value is higher than the best leakage currents achieved by pulsed laser processing but represents a significant improvement when compared to other cw laser experiments (see Table 1.3). The reverse leakage current for higher bias conditions, (shown in Fig. 6.8) can not be compared with other results since no data are available.

6.4 Junction Capacitance

The capacitance C of the p-n junction as a function of the reverse voltage was also measured. According to theory for an ideal one-sided step junction a plot of $1/C^2$ vs. bias voltage is linear. Since the measured curve, shown in Fig. 6.9, exhibits this linear relationship it indicates an abrupt change in doping level at the junction, in agreement with the expected confinement of phosphorus within the melted zone. The slope of this curve is consistent with the known substrate doping.

6.5 Lateral NPN Transistor

To demonstrate the possibility of maskless processing using a "laser writing" technique, a lateral bipolar transistor was made simply by laser processing two separate lines, leaving a small gap between them. This process results in two separate n-type diffused

Figure 6.9 C-V measurement of a junction formed by the cw laser-induced diffusion.

regions (emitter and collector) in the p-type substrate (base). The characteristics of this device are shown in Fig. 6.10. Although this very simple process results in only poor transistor characteristics, - as a direct consequence of the wide base region and the high density of generation-recombination centers - the transistor action observed also confirms the formation of p-n junctions by the cw laser-processing. In order to fully explore this possibility, a much smaller beam diameter and a scanning system with a higher resolution must be employed.

Figure 6.10 Characteristics of a lateral npn transistor fabricated by the localized cw laser-induced diffusion process without using any masks.

CHAPTER 7

CONCLUSION AND FURTHER WORK

This final chapter is intended to summarize the main results of this thesis, point out those which are considered to be novel and also to assess their importance. Remaining problems will also be discussed leading to suggestions for further works.

7.1 Conclusion

This thesis discussed the feasibility of forming shallow diffusions in silicon via a laser-induced liquid phase diffusion process using a cw argon ion laser. While the laser-induced diffusion process offers many advantages over other diffusion processes (the possibility of forming very shallow diffusions, localized processing, and high dopant concentration), there are also difficulties, such as the controllability of the process and the introduction of damage during processing. These have to be dealt with before this process can be used for semiconductor device fabrication.

A theoretical investigation of the heat flow during laser processing was carried out to predict the dependence of the

temperature rise and melt depth on the processing parameters. The numerical model developed to solve for the first time the time-dependent heat flow problem in the case of cw laser processing including the effects of melting, is a novel result of the thesis. From the results of this analysis it was concluded that high speed scanning of the beam improves the controllability of the process.

A review of the various mechanisms which can lead to the introduction of damage into the silicon, with special attention to liquid flow, also showed the advantage of high speed scanning of the laser beam. Based on these considerations a novel technique was developed to carry out the laser processing, which includes (a) high speed scanning of the cw laser beam to melt a thin surface layer of the silicon, and (b) application of a phosphosilica glass as a diffusion source which also serves as an antireflective coat thereby ensuring selective processing while protecting the other parts of the circuit during scanning. The beam scanner designed to provide optimum processing conditions is also a new development in the sense that it combines the advantages of the two previously applied beam scanning techniques.

The processing sequence used to fabricate p-n junction diodes for testing this novel cw laser-induced diffusion process is described. The crucial steps of this process are (a) the deposition of the PSG diffusion source with the appropriate thickness to produce the desired AR affect, (b) the raster scanning of the laser beam to

cover uniformly the silicon surface and (c) the selection of the appropriate laser power which melts a continuous thin silicon layer without introducing a significant amount of crystal damage. Since this diffusion technique produces shallow diffusions it was necessary to prevent the interdiffusion of silicon and the aluminum used as contact metal. For that purpose a tungsten silicide barrier layer was formed which resulted in a reliable contact to the shallow diffusion.

The experimental results proved that good quality p-n junctions with leakage currents in the order of 5×10^{-6} A/cm² and junction depths in the range of 0.2-0.4 μ m can be formed using cw laser-induced diffusion technique. The junction depth measurements showed good agreement with the numerically calculated dependence of the melt depth on the laser power and scanning speed. It was also shown that only high speed scanning of the laser beam can produce relatively damage free surfaces when surface melting is carried out with a cw laser.

The measured leakage current is lower than reported for other cw laser-induced diffusion experiments, so that for the first time good quality diodes have been formed by cw laser-induced diffusion.

For those devices with poorer diode characteristics, the main problems are the nonuniformity of the melting when low laser power is used, and the crystal damage introduced at higher laser powers. This explains why the best diodes have junction depths between 0.2-0.4 μ m.

For shallower melt depth the width of the melted line is not enough to ensure that a continuous junction is formed between adjacent lines, while processing with higher laser power, which can produce deeper melting, introduces damage. Fortunately this second observation does not pose serious restriction on this technique since the aim is to form shallow diffusions. The first problem can be readily solved by either placing the scan lines closer thus providing more overlapping or increasing the spot size which requires more laser power. Although the leakage current presently achieved is higher than the best results achieved by either pulsed laser or standard ion implantation processes, it is expected, based on this consideration, that refinement of the process can further improve the quality of the junction.

Finally it can be concluded that the cw laser-induced diffusion technique can be used to form good quality shallow diffusions. This result can open up a new area of research which can benefit from the advantage of the cw laser processing as was discussed earlier. The quality of this junction is expected to improve by improving the processing conditions. This technique can be valuable if localized and/or low temperature processing is essential, to form device structures difficult to achieve by other techniques.

7.2 Future Work

As it was pointed out earlier it is expected that these results on ~~low~~ laser-induced liquid phase diffusion can initiate further research in this field. The direction of this work can include the following areas.

The numerical model developed to solve the time dependent heat flow problem for the cw laser-induced melting process can be further developed to include structures such as thin amorphous or polycrystalline silicon on either single crystal silicon or insulators by choosing the appropriate boundary conditions and including the optical and thermal properties of these materials.

It was mentioned earlier that the relatively high sheet resistance obtained is due to the particular diffusion source used. The dopant concentration can be increased by using other deposition techniques such as evaporation in vacuum to form a thin layer of the desired impurity on the silicon surface which then can be covered by the silica glass layer to obtain the AR effect. This technique can increase the dopant concentration even above the solid solubility limit, and also extend the application of this diffusion technique to other dopants. To obtain a glass layer with better uniformity, the Low Pressure CVD (LPCVD) technique can be employed.

The quality of the junction can be improved by increasing the overlapping between adjacent scan lines or increasing the spot size.

The control over the scanning process can also be improved by minimizing scanning errors introduced by the mechanical vibration of the system. It is expected that in this way even shallower diffusions with lower leakage current can be formed.

The resultant dopant concentration can be determined by using either SIMS or RBS techniques. This result then can be used to obtain more information about the details of the liquid phase diffusion process.

The improved process can be used to fabricate semiconductor devices or integrated circuits where the unique features of this technique allow the formation of improved or novel device structures. One of the many possibilities is the direct writing technique which relies on the localized nature of laser processing. Using this method the diffusion pattern is written into the silicon without the use of a complicated photolithography process, by controlling the intensity of the laser beam during scanning.

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APPENDIX A

LISTING OF PROGRAM FOR HEAT FLOW SIMULATION

```

C      THIS PROGRAM SOLVES THE NONLINEAR
C      HEAT TRANSPORT EQUATION
C
C      Input parameters received from the terminal:
C      laser power, backsurface temperature, scanning velocity,
C      antireflective coat
C
C      Results are stored in files on the following unit numbers:
C      result.....102 unit number
C      temperature profile ...103      "
C      test.....105      "
C
C      *****
C
C      PROGRAM DIFF
C
C      declaration of variables
C
C      INTEGER NUMIT,ITLIM,NP,AR,IFLAGR,IFLAGM
C      NUMIT,ITLIM .... number of iterations, maximum number
C                        of iterations
C      NP ..... number of grid points
C      AR ..... 0 or 1 depending on whether antireflective
C                        coat is used
C      IFLAGR,IFLAGM .. 0 or 1 depending on the progress of the
C                        iteration
C
C      DOUBLE PRECISION T(90),TE(90),HENGTE(90),HENGTE(90),
C      T,TE ..... temperature, temperature at the advanced time
C                        level
C      HENGTE,HENGTE ... heat energy, heat energy at the advanced time
C                        level
C      $RHS(90),DFTE(90),DFTEM(90),DFTEP(90),P(90),R(90),DHENG(90),
C      RHS ..... right hand side of the eq. system,
C                        or the solution
C      DFTE,DFTEM,DFTEP... elements of the tridiagonal matrix
C      $HCAP(90),HDIFT(90),TM,RT,RTE0,RTE,DM,DRT,DRPDT,TEINC,DT(90),
C      HCAP,..... heat capacitance
C      TM,DM ..... melting temperature, depth of melt

```

```

C      RT,RTE,RTEO .... reflectivity
      $DT1,DT2,AVC1,AVC2,RTEP,ERTE,RTET,RTEP0,RM,
      $ABSRT(90),HCON(90),DHCON(90),ABSO,DRPDTE,DLTHD,
C      ABSRT,ABSO ..... energy absorption (heat source)
C      HCON,DHCON ..... heat conductivity, and derivative
      $X(90),DX(90),DDX(90),LTHD(90),HLTHD(90),RHSN(90),
C      X,DX,DDX ..... grid points, spacings
C      LTHD ..... lateral heat diffusion
      $DTEMP,DTIME,TIME,MAXT,TIME0,W,FPW2,AREA,LDIF,
C      DTIME,TIME,MAXT. time step, time, maximum time
C      W,AREA ..... 1/e radius of the laser beam, area
      $FINC,MAGN,Q0,HF,TJ,TBL,DTEM,DTEO,TEO,DMS,
C      HF,TBL ..... latent heat of fusion, backsurface temperature
      $VELOCI,POWER0,DMRL,DMO,DMP,DDM,DDMO
C      VELOCI ..... scanning velocity
C
      REAL TEMPP(90,6)
C      TEMPP ..... temperature profiles at different instants
      DATA ((TEMPP(I,J),I=1,90),J=1,6)/540*0.0/
C
C      common blocks
C
      COMMON/EQN/ DFTE,DFTEM,DFTEP,RHS,P,R
      COMMON/ABSRP/ ABSRT
      COMMON/HEATSP/ VELOCI,POWER0,W
      COMMON/HPAR/ HENGTE,HCAP,HCON,DHCON
      COMMON/MELT/ X,DX
      COMMON/TEMPR/ TE
      GLOBAL TM,HF,TJ,TD,AR,DMRL,NP
C
C      parameters to determine grid spacings
      Q0=2./30.; MAGN=60.0
C
C      constants
      TM=1690.D0;HF=3271.D0;W=20.D-4;DMRL=2.5D-6;TJ=1.D0;TD=8.D0
      DMP=0.D0;DDM=0.D0
      NP=90
      FPW2=4.D0/W**2
      AREA=W**2*3.14159D0
C
C      interactive program to receive parameters
      WRITE(6,*) 'POWER, TEMPR, SCANNING VEL, AR:'
      READ(5,'(4E20.10)') POWER0,T(NP),VELOCI,AR
      TE(NP)=T(NP)
      TBL=T(NP)
C
C      set up grid points
C
      DX(1)=5.D-7
      X(1)=-DX(1)
      DO 10 N=2,NP

```

```

X(N)=X(N-1)+DX(N-1)
  Q=Q0+MAGN*K(N)
10  DX(N)=DX(N-1)*(1.D0+Q),
  C
  DO 15 N=2,NP-1
15  DDX(N)=2.D0/(DX(N)+DX(N-1))
  C
  C      starting values
  C
  MAXT=0.D0;MLIM=0;MDISP=2;ITLIM=20;NUMIT=10;RM=-1.D0
  TIME=0.D0;DTIME=3.D-9;DTEMP=10.D0;TIME0=0.D0;DRT=0.D0
  DRPDT=0.D0; DRPDTE=4.29D-5; NUMTL=15; DM=0.D0
  C
  DO 20 N=2,NP
  T(N)=T(NP)
  HENGT(N)=2.2D0*T(NP)
  HCAP(N)=2.2D0
  HCON(N)=0.5D0
  HLTHD(N)=0.D0
  LTHD(N)=0.D0
  HDIFT(N)=0.D0
  ABSRT(N)=0.D0
20  RHSN(N)=0.D0
  RT=REFL(T(2),0.D0)
  C
  C      computation starts /M number of iterations/
  C
  M=0
40  M=M+1
  C
  IF(M.LE.MLIM) GOTO 41
  MDISP=M
  WRITE(105,101)
  $M-1,NUMT,NUMIT,1.E6*TIME,TE(2),DDX(2)*HDIFT(2),
  $(1.-RTE)*ABSRT(2),HCON(2)*LTHD(2),DTIME,1.E4*DM
  C
  C      receives maximum number of iteration / MLIM/
  C
  WRITE(6,*) 'MAX NUM OF TIME STEPS /MLIM/?'
  READ(5,'(I5)') MLIM
  IF(MLIM.EQ.0) GOTO 300
41  IF(TIME.LT.MAXT) GOTO 42
  C
  C      receives maximum time /MAXT/
  C
  WRITE(6,*) 'MAX TIME /MAXT/?'
  READ(5,'(E20.10)') MAXT
  IF(MAXT.EQ.0.D0) GOTO 300
42  IF(M.NE.MDISP) GOTO 43
  MDISP=M+20
  C

```

```

C      displays intermediate results
C
WRITE(6,102) M-1,1.E6*TIME,TE(2),1.E4*DM,DTIME
C
C      time step /DTIME/ adjustment according to the
C      range of temperature and speed of iteration
C
43  TEINC=10.D0
    IF(T(2).GT.TM-TD-2.D0*TJ) TEINC=2.D-1
    IF(T(2).GT.TM) TEINC=5.D-3
    IF(DM.GT.DMRL) TEINC=0.5D0
    FINC=MIN(MAX(0.5,FLOAT(ITLIM)/NUMIT),2.)
    FINC=DMIN(TEINC/DTEMP,FINC)
    FINC=DMIN(FINC,2.D-3/DABS(DRT))
    FINC=DMIN(FINC,3.D-7/DMAX(DDM,1.D-7))
    DTIME=DMIN(DTIME*FINC,1.D-6)
C
C      solves the (3.6a) differential equation
C      to calculate T(z,t,r=0)
C
C      first approximation using explicite method
C
    DO 50 N=2,NP-1
50   DHENG(N)=(DDX(N)*HDIFT(N)+(1.D0-RT)*ABSO*ABSRT(N)+
$HCON(N)*LTHD(N))/HCAP(N)
C
60   DO 61 N=2,NP-1
61   TE(N)=DTIME*DHENG(N)+T(N)
    RTE=DRPDT*DTIME+RT
    IF(DABS(RTE-RT).GT.2.D-3) DTIME=DTIME/1.2; GOTO 60
C
C      iteration starts to determine the temperature at the
C      advanced time level (TE)
C
    IF(DTIME.GT.1.D-12) GOTO 62
    DM=DMELT()
    RTE=REFL(TE(2),DM)
    GOTO 200
C
62   NUMIT=0
    ABSO=POWER(TIME+DTIME)/AREA
    DTEM=1.D4; IFLAGR=0
C
70   NUMIT=NUMIT+1
    IFLAGM=0
    IF(NUMIT.GT.ITLIM+15) DTIME=DTIME/2.; GOTO 60
C
C      calculate the matrix elements
C
    IF((DTEM.LT.5.D-3).AND.(NUMIT.GT.2)) IFLAGM=1
C

```

```

C          calculate heat conductivity and total heat at TE
C
CALL ENGCON
C
C          calculate the absorbed heat at TE
IF((DTEM.GT.5.D-3).AND.(DM.LT.1.5D0*DMRL)) CALL ABSR
C
AVC2=0.5D0*(HCON(2)+HCON(3))
DT2=(TE(2)-TE(3))/DX(2)
DO 80 N=2,NP-1
AVC1=AVC2; AVC2=0.5D0*(HCON(N)+HCON(N+1))
DT1=DT2; DT2=(TE(N+1)-TE(N))/DX(N)
HDIFT(N)=AVC2*DT2-AVC1*DT1
RHS(N)=HENGTE(N)-HENGTE(N)+DTIME*(DDX(N)*HDIFT(N)+
$      (1.D0-RTE)*ABS0*ABSRT(N)+HCON(N)*LTHD(N))
IF(IFLAGM.EQ.1) GOTO 80
DFTEM(N)=DDX(N)*DTIME*(AVC1/DX(N-1)-0.5D0*DHCON(N-1)*DT1)
DFTEP(N)=DDX(N)*DTIME*(AVC2/DX(N)+0.5D0*DHCON(N+1)*DT2)
DFTE(N)=HCAP(N)+DTIME*(DDX(N)*
$(AVC1/DX(N-1)+AVC2/DX(N)+0.5D0*DHCON(N)*(DT1-DT2))
$-DHCON(N)*LTHD(N))
80  CONTINUE
IF(IFLAGM.NE.1) DFTEP(2)=DFTEP(2)+DFTEM(2)
C
C          calculates the maximum error /DRHS/
DRHS=0.D0
DO 81 N=2,NP-1
81  IF(DABS(RHS(N)).GT.DRHS) DRHS=DABS(RHS(N)); NCR=N
C
C          solves the equation system /result is in RHS/
CALL SOLEQN(IFLAGM)
C
C          determines the maximum temperature change
DTEM=0.D0
DO 90 N=2,NP-1
IF(DABS(RHS(N)).GT.DTEM) DTEM=DABS(RHS(N)); NCT=N
C
C          new approximation of the temperature TE
90  TE(N)=TE(N)+RHS(N)
C
RTEP=RTE
C
C          calculates the melt depth and reflectivity
DM=DMELT()
RTE=REFL(TE(2),DM)
C
C          stores intermediate results to test the iteration
IF(MLIM.EQ.2) WRITE(105,103) NUMIT,NCR,NCT,TE(NCT),DRHS,DTEM,
$RTE,RTEP,1.E4*DM,RM,DTIME,IFLAGM

```

```

C      ERTE=DABS(RTE-RTEP)
C
C      determines whether iteration has to be used to calculate
C      the reflectivity
C      IF((DTEM.LT.5.D-8).AND.(ERTE.LT.DMAX(1.D-3*DABS(RTE-RT),1.D-8)))
$      GOTO 100
C
C      IF((TE(2).LT.TM-1.D0).OR.(DM.GT.1.5D0*DMRL)) GOTO 70
C
C      IF(DMAX(DABS(RTE-RTET),DTEM).LT.DMAX(5.D-2*ERTE,1.D-5))
$      GOTO 95
C      RTET=RTE
C      RTE=RTEP
C      GOTO 70
C
C      Newton's iteration to calculate reflectivity
C
C      95 IF(IFLAGR.EQ.1) RM=(RTE-RTE0)/(RTEP-RTEP0)
C      RTE0=RTE; RTEP0=RTEP
C      RTET=RTE
C      RTE=(RTE-RM*RTEP)/(1.D0-RM)
C      IFLAGR=1
C      GOTO 70
C
C      iteration completed
C
C
C      solves the (3.6b) differential equation to calculate
C      the lateral heat diffusion /LTHD/ at r=0
C
C      100 DO 121 N=NP,2,-1
C      121 IF(TE(N)-TBL.LT.1.D0) NL=N
C      NP=NL
C      DRPDTE=(RTE-RT)/(TE(2)-T(2))
C      DO 122 N=2,NP-1
C      DT(N)=TE(N)-TBL
C      122 IF(TE(N).GT.TM) DT(N)=DMAX(TE(N)-TM,1.D0)
C
C      first approximation using explicite method
C
C      DO 123 N=2,NP-1
C      123 LTHD(N)=(HLTHD(N)+DTIME*RHSN(N))/HCAP(N)
C
C      NUMT=0; IFLAGM=0
C      DLTHD=1.0D10
C      130 NUMT=NUMT+1
C
C      calculates the matrix elements
C
C      IF(DLTHD.LT.5.D-2*DABS(LTHD(2))) IFLAGM=1

```



```

AVC2=0.5D0*(HCON(2)+HCON(3))/DX(2)
DT2=(LTHD(2)-LTHD(3))
DO 140 N=2,NP-1
AVC1=AVC2; AVC2=0.5D0*(HCON(N)+HCON(N+1))/DX(N)
DT1=DT2; DT2=(LTHD(N+1)-LTHD(N))
LDIF=(AVC2*DT2-AVC1*DT1)*DDX(N)
RHSN(N)=LDIF+2.D0*HCON(N)/DT(N)*LTHD(N)**2
$      -((1.D0-RTE)*FPW2+DRPDTE*LTHD(N))*ABS0*ABSRT(N)
RHS(N)=HLTHD(N)-LTHD(N)*HCAP(N)+DTIME*RHSN(N)

C
      IF(IFLAGM.EQ.1) GOTO 140
      DFTEM(N)=DDX(N)*DTIME*AVC1
      DFTEP(N)=DDX(N)*DTIME*AVC2
      DFTE(N)=HCAP(N)+DFTEM(N)+DFTEP(N)+
$      DTIME*(-4.D0*HCON(N)/DT(N)*LTHD(N)+DRPDTE*ABS0*ABSRT(N))
140  CONTINUE
      IF(IFLAGM.NE.1) DFTEP(2)=DFTEP(2)+DFTEM(2)

C
C      solves the equation system for LTHD /result in RHS/
C
      CALL SQLEQN(IFLAGM)

C
C      determines the maximum error
      DLTHD=0.D0
      DO 150 N=2,NP-1
      LTHD(N)=LTHD(N)+RHS(N)
150  IF(DABS(RHS(N)).GT.DLTHD) DLTHD=DABS(RHS(N)); NR=N
C
      IF(MLIM.EQ.2) WRITE(105,104) NUMT,NR,NTS,LTHD(2),DLTHD,DRPDTE

C
C      checks the error
      IF(DLTHD.GT.1.D-8*DABS(LTHD(2))) GOTO 130
      DO 160 N=2,NP-1
160  HLTHD(N)=LTHD(N)*HCAP(N)
      IF(MLIM.EQ.2) WRITE(105,'(4(X,10E9.3,/))')
$      (LTHD(J), J=2,80,2)
      NP=90

C
C      iteration completed for LTHD
C
200  TIME=TIME+DTIME
      DO 210 N=2,NP-1
210  HENGT(N)=HENGTE(N)
C
      BDM=DABS(DM-DMP)
      DRT=RTE-RT
      DTEMP=DABS(TE(2)-T(2))
      DRPDTE=DRT/DTIME
      DMP=DM
      RT=RTE

```

```

DO 220 N=2,NP-1
220 T(N)=TE(N)
C
C
C      stores results
C
IF(MLIM.GT.6) GOTO 245
DO 230 N=2,NP
230 TEMPP(N,MLIM)=TE(N)
245 DDMO=DABS(DM-DMO)
DTEO=DABS(TE(2)-TEO)
DMS=3.D-7
IF(DM.GT.3.*DMRL) DMS=5.D-6
IF((DDMO.LT.DMS).AND.(DTEO.LT.5.D1).AND.(TIME.LT.TIMEO)) GOTO 40
TEO=TE(2); DMO=DM; TIMEO=TIME+5.D-6
PW=POWER(TIME); DIST=(VELOCI*TIME-W)*1.E4
WRITE(102,105) 1.E6*TIME,TE(2),1.D4*DM,(1.-RTE)*PW,PW,DIST
C
GOTO 40
C
300 CONTINUE
C
DO 310 N=2,NP
310 WRITE(103,106) 1.E4*X(N),(TEMPP(N,L),L=1,6)
C
C      format statements
101 FORMAT(X,3I5,F7.3,F7.1,3E12.5,E9.2,F7.4)
102 FORMAT(X,I5,2X,'TIME:',F8.3,2X,'TE:',F11.5,2X,'DM:',
$F8.4,2X,'DTIME:',E7.1)
103 FORMAT(X,3I3,F16.10,2E9.2,3F11.8,E10.3,E8.2,I2)
104 FORMAT(10X,3I3,3E11.4)
105 FORMAT(X,F7.3,F7.1,F7.4,3F7.2)
106 FORMAT(X,7F12.4)
C
END
C
C
C      SUBROUTINES AND FUNCTIONS
C
C      SUBROUTINE ENGCON
C
C      This subroutine calculates the heat conductivity,
C      total heat and also their derivatives at temperature T
C
C      DOUBLE PRECISION TM,T(90),HENG(90),HCAP(90),HCON(90),
C      SDHCON(90),ET,EET,TD,TJ
C      COMMON/HPAR/ HENG,HCAP,HCON,DHCON
C      COMMON/TEMPR/ T
C      GLOBAL TM,TD,TJ,HF,NP
C

```

```

DO 10 N=2,NP
HENG(T(N)=2.2D0*T(N)
HCAP(N)=2.2D0
HCON(N)=299.D0/(T(N)-99.D0)
DHCON(N)=-1.D0*HCON(N)/(T(N)-99.D0)

```

```

C      ET=(TM-TD-T(N))/TJ
      IF(DABS(ET).GT.25.D0) GOTO 15
      EET=DEXP(ET)
HENG(T(N)=HENG(T(N)+HF/(EET+1.D0)
HCAP(N)=HCAP(N)+HF/TJ*EET/(EET+1.D0)**2
HCON(N)=HCON(N)+0.5D0/(EET+1.D0)
DHCON(N)=DHCON(N)+0.5D0/TJ*EET/(EET+1.D0)**2

```

```

C
15  IF(ET.GT.-25.D0) GOTO 10
    HCON(N)=HCON(N)+0.5D0
    HENG(T(N)=HENG(T(N)+HF
10  CONTINUE

```

```

C
    HCON(1)=HCON(3)
    DHCON(1)=DHCON(3)
    RETURN
    END

```

```

C
C
C
C

```

SUBROUTINE ABSR

```

C      This subroutine calculates the absorbed heat distribution
C      at temperature T
C

```

```

    DOUBLE PRECISION TE(90),TS,TM,ABSRT(90),X(90),DX(90),
$ALFA1,ALFA2,ALFX
    COMMON/ABSRP/ ABSRT
    COMMON/TEMPR/ TE
    COMMON/MELT/ X,DX
    GLOBAL TM,NP

```

```

C
    N=1
1  N=N+1
    TS=TE(N)
    ALFA1=ALFA2
    IF(TS.LT.TM) ALFA2=7.5D3*DEXP(TS/452.D0)
    IF(TS.GE.TM) ALFA2=3.15399810479D5+DMIN(TS-TM,0.5D0)/0.5D0*1.75D5
    ALFX=ALFX+5.D-1*(ALFA1+ALFA2)*DX(N-1)
    IF(N.EQ.2) ALFX=0.D0
    IF(ALFX.GT.15.D0) GOTO 10
    ABSRT(N)=ALFA2*DEXP(-ALFX)
    GOTO 1
10  DO 20 J=N,NP-1

```

```

20  ABSRT(J)=0.D0
    RETURN
    END

```

```

C
C
C
C

```

```

SUBROUTINE SOLEQN(IFLAGM)

```

```

C
C
C
C
C

```

```

    This subroutine solves the equation system for a
    tridiagonal matrix A,B,C the right hand side is D,
    the result is stored in D

```

```

    DOUBLE PRECISION A(90),B(90),C(90),D(90),
    *P(90),S(90),R(90)

```

```

C

```

```

    COMMON/EQN/ B,A,C,D,P,R
    GLOBAL NP

```

```

C

```

```

    P(2)=B(2)
    S(2)=D(2)

```

```

C

```

```

    DO 20 N=3,NP-1
        IF(IFLAGM.EQ.1) GOTO 10
        R(N)=A(N)/P(N-1)
        P(N)=B(N)-R(N)*C(N-1)
        S(N)=D(N)+R(N)*S(N-1)
10    CONTINUE
20

```

```

C

```

```

    D(NP-1)=S(NP-1)/P(NP-1)
    DO 30 N=NP-2,2,-1
30    D(N)=(S(N)+C(N)*D(N+1))/P(N)

```

```

C

```

```

    RETURN
    END

```

```

C
C
C

```

```

DOUBLE PRECISION FUNCTION POWER(T)

```

```

C
C
C
C

```

```

    This function calculates the laser power
    at the time instant T

```

```

    DOUBLE PRECISION T,VELOC,POWER0,W,S
    COMMON/HEATSP/ VELOC,POWER0,W

```

```

C

```

```

    IF(VELOC.EQ.0.D0) GOTO 10
    S=(T*VELOC/W-1.D0)**2
    IF(S.GT.5.D1) GOTO 20
    POWER=POWER0/EXP(S)
    RETURN

```

```

10  POWER=POWER0
    RETURN
20  POWER=0.D0
    RETURN
    END

```

C
C
C
C
C
C

```
DOUBLE PRECISION FUNCTION REFL(T,DM)
```

C
C
C
C

```

    This function calculates the reflectivity
    at temperature T, with or without antireflective coat

```

```

DOUBLE PRECISION T,DM,RMIN,RMAX,TM,DMRL,ET
INTEGER AR
GLOBAL TM,DMRL,AR

```

C

```

RMIN=0.367D0; RMAX=0.28D0
IF(AR.EQ.1) RMIN=0.147D0;RMAX=0.296D0

```

C

```

REFL=RMIN+4.29D-5*DMIN(T,TM)
    ET=(DMRL/2.D0-DM)/DMRL*6.D0
    IF(DABS(ET).GT.20.D0) GOTO 5
REFL=REFL+RMAX/(DEXP(ET)+1.D0)
5  IF(ET.LE.-20.D0) REFL=REFL+RMAX
    RETURN
    END

```

C
C
C

```
DOUBLE PRECISION FUNCTION DMELT()
```

C
C
C
C
C

```

    This function determines the melt depth
    by fitting a forth order polinomial on the
    temperature values around the melting point

```

```

DOUBLE PRECISION T(90),TM,X(90),DX(90),
$IT(3),D(3),A(3,3),V(3),DET(4),TE,DTE,S,DS
COMMON/MELT/ X,DX
COMMON/TEMPR/ T
GLOBAL TM

```

C

```

L=1
1  L=L+1
    IF(T(L).GT.TM) GOTO 1
    DMELT=0.D0
    IF(L.EQ.2) GOTO 100
    DMELT=X(L-1)+DX(L-1)*(T(L-1)-TM)/(T(L-1)-T(L))

```

```

      IF(L.EQ.3) GOTO 101
C
      DO 10 I=1,3
      TT(I)=T(L-2+I)-T(L-2)
10     D(I)=X(L-2+I)-X(L-2)
C
      DO 30 N=1,4
      DO 20 K=1,3
      DO 20 M=1,3
      IF(M.EQ.N) A(K,M)=TT(K)
20     IF(M.NE.N) A(K,M)=D(K)**M
C
      DET(N)=A(1,1)*(A(2,2)*A(3,3)-A(3,2)*A(2,3))
      S-A(1,2)*(A(2,1)*A(3,3)-A(3,1)*A(2,3))
      S+A(1,3)*(A(2,1)*A(3,2)-A(3,1)*A(2,2))
C
      DO 40 I=1,3
40     V(I)=DET(I)/DET(4)
C
      ( Newton's iteration
C
      S=DMELT-X(L-2); DS=0.D0
50     S=S+DS
      TE=T(L-2)+V(1)*S+V(2)*S**2+V(3)*S**3
      IF(DABS(TE-TM).LT.1.D-7) GOTO 60
      DTE=V(1)+2.D0*V(2)*S+3.D0*V(3)*S**2
      DS=(TM-TE)/DTE
      GOTO 50
60     DMELT=X(L-2)+S
100    RETURN
101    DMELT=DSQRT((T(2)-TM)/(T(2)-T(3)))*DX(2)
      END

```

APPENDIX B

LISTING OF PROGRAM FOR SCANNER CONTROL

Listing of the assembly language program and machine code which controls the motion of the vibrating mirror and the translating stage through the respective driver units. The beam is raster scanned by synchronizing the motion in the x and y directions (for details see timing diagrams in section 4.2.2). The width of the scanned area is controlled by the content (m) of memory register 15. (width = $m \times 0.5$ mm). The number of repetition is determined by the content of memory register 20. The program is stored on a audio tape with title 44.

ADDRESS	MNEM.	OP CODE	COMMENTS
0200	LDA	A9 00	Initialization
0202	STA	8D FA 17	.
0205	LDA	A9 1C	.
0207	STA	8D FB 17	.
020A	NOP	EA	.
020B	NOP	EA	.
020C	LDA	A9 FF	Defines I/O memory locations
020E	STA	8D 01 17	.
0211	LDA	A9 FE	1700: A0...A7 Output
0213	STA	8D 03 17	1702: B0 Input; B1...B7 Output
0216	NOP	EA	.
0217	LDA	A9 10	Codes for stepping motor
0219	STA	85 00	A7: Step
021B	LDA	A9 11	A6: Direction
021D	STA	85 01	A5: X or Y motor
021F	LDA	A9 14	.
0221	STA	85 02	.
0223	LDA	A9 15	.
0225	STA	85 03	.
0227	NOP	EA	.
0228	LDA	A9 0A	Default width of scan (x 0.5 mm)
022A	STA	85 15	.
022C	LDA	A9 00	Initialize registers
022E	STA	85 13	.
0230	STA	85 14	.
0232	STA	85 18	.
0234	STA	85 19	.
0236	LDA	A9 02	Default no. of repetitions
0238	STA	85 20	.
023A	NOP	EA	.
023B	NOP	EA	.
023C	NOP	EA	.
023D	LDA	A9 00	Enable off
023F	STA	8D 02 17	.
0242	NOP	EA	 Receives sync. signal....
0250	LDA	A9 FE	B1=1 enable on
0252	STA	8D 02 17	.
0255	NOP	EA	.
0256	LDA	A9 01	Delay 1ms
0258	JSR	20 D0 02	.
025B	NOP	EA	.
02DC	LDA	A9 00	B1=0 enable off
02DE	STA	8D 02 17	.
0261	NOP	EA	.
0262	LSR	4E 02 17	Checks if B0=1
0265	BCC	90 FB	If B0=1 then continues

ADDRESS	MNEM.	OP CODE	COMMENTS
0267	NOP	EA	
0240	LDA	A9 03	Delay 3 ms
026A	JSR	20 D0 02	.
026D	NOP	EA	
026E	INC	E6 13	Counts no. of scans
0270	LDA	A9 50	.
0272	CMP	C5 13	If equal to mem. 15 stop
0274	BEQ	F0 03	.
0276	JMP	4C B0 02	.
0279	LDA	A9 00	.
027B	STA	85 13	.
027D	INC	E6 14	.
027F	LDA	A5 14	.
0281	CMP	C5 15	.
0283	BEQ	F0 03	.
0285	JMP	4C B0 02	.
0288	LDA	A9 00	.
028A	STA	85 14	.
028C	INC	E6 19	.
028E	LDA	A5 19	.
0290	CMP	C5 20	.
0292	BEQ	F0 03	.
0294	JMP	4C A0 02	.
0297	BRK	00	.
0298	NOP	EA	
02A0	LDA	A9 10	Changes direction
02A2	EOR	45 00	.
02A4	STA	85 00	.
02A6	LDA	A9 10	.
02A8	EOR	45 01	.
02AA	STA	85 01	.
02AC	NOP	EA	
02B0	LDA	A5 01	Moves one step
02B2	STA	8D 00 17	.
02B5	LDA	A9 01	.
02B7	JSR	20 D0 02	.
02BA	LDA	A5 00	.
02BC	STA	8D 00 17	.
02BF	NOP	EA	
02C0	LDX	A2 02	Starts again the cycle
02C2	LDA	A9 14	After delay of 25 ms

ADDRESS	MNEM.	OP CODE	COMMENTS
02C4	JSR	20 D0 02	.
02C7	DEX	CA	.
02C8	BNE	D0 F8	.
02CA	JMP	4C 50 02	.
02CD	NOP	EA	.
02D0	STA	85 23	Subroutine delay
02D2	LDA	A9 00	.
02D4	STA	85 22	Delay=accumulator x 1 ms
02D6	LDA	A9 00	.
02D8	STA	85 21	.
02DA	INC	E6 21	.
02DC	INC	E6 EE	.
02DE	DEC	C6 EE	.
02E0	LDA	E5 21	.
02E2	CMP	C9 2D	.
02E4	BNE	D0 F4	.
02E6	INC	E6 22	.
02E8	LDA	A5 22	.
02EA	CMP	C5 23	.
02EC	BNE	D0 EA	.
02EE	RTS	60	Return

APPENDIX C

DETAILED FABRICATION SCHEDULE OF DIODES

1. Wafers:

- 2 inch diameter, p type (100) orientation silicon wafers
- scribe identification numbers on front

2. Prefurnace clean:

- 15 minutes in a mixture of 400 ml DI water, 80 ml hydrogen peroxide (H_2O_2), and 80 ml ammonium hydroxide (NH_4OH) at 80 C
- 10 minutes rinse in flowing DI water
- 15 minutes in 400 ml DI water, 80 ml H_2O_2 and 80 ml HCl at 80 C
- 15 minute rinse in flowing DI water
- 2 minute etch in 10% hydrofluoric acid (HF)
- 15 minute rinse in DI water, blow dry with nitrogen (N_2)

3. Oxidation (to grow thick oxide):

- 2 hour purge to getter the furnace with O_2 and HCl at 1150 C
- furnace temperature set at 1100 C
- load slices on boat, allow a 5 minute warm up in O_2
- 2 minute push in, 10 minutes in O_2 , 3 hours in H_2 and O_2 ,
30 minutes in O_2 and 2-5% HCl oxidation
- 40 minute anneal in H_2
- 5 minute pull out

4. Photolithography (to define diode area):

- 2 hour prebake at 350 C
- spin positive photoresist on front
- 30 minute bake at 105 C
- align mask and expose (3 sec)
- develop, dry in alcohol
- 30 minute post bake at 130 C
- etch oxide in buffered HF, 10 minute rinse in DI water
- strip photoresist in Caro's acid, 10 minute DI rinse

5. Phosphosilicate glass deposition (for diffusion source):

- purge Silox reactor set temperature at 350 C
- flash etch wafer in buffered HF for 5 sec., 10 minute DI rinse
immediately before loading into the reactor
- load wafer on quartz plate, 3 minute warm up in N_2

- 3 minute 40 second run in O_2 (150 ml/min), silane (SiH_4) (24 ml/min), phosphine PH_3 (6 ml/min) and N_2 (40 l/min)
the colour of the 250 nm PSG is melon-orange
- 5 minutes in only N_2
- /- remove wafer and measure oxide thickness using ellipsometer

6. Laser processing (to drive-in phosphorus):

- turn on chuck heater (takes 2-3 hours to reach 330 C)
- start CR-18 argon ion laser refer to laser manual (water cooling, N_2 purge, delays, alignment of laser mirrors)
- set laser power less than 0.5 W and check the alignment of beam scanner mirrors and lens
- load scanner program (44) from cassette (starting address 200)
- place wafer on sample holder, align beam to the edge of the area to be annealed
- set scan length and scan time to 100 cm/s
- set output laser power to approx. 8.5 W (60 mV on the digital power meter), (repeated alignment of the laser mirrors and adjustment of laser current is necessary after the stabilization of the output power)
- scan the desired area
- inspect wafer

7. PSG etch:

- approx. 3 minutes in Siloxide etch
- 10 minute rinse in DI water, blow dry with N₂

8. Undoped oxide deposition:

- same as 5. except without PH₃
- 6 minutes in O₂ (150 ml/min) SiH₄ (30 ml/min) N₂ (40 l/min)
colour of 500 nm oxide is yellow-green

9. Photolithography (to open contact window)::

- same as 4. except using contact mask and Siloxide to etch
silica glass
- etch time 4 minutes, inspect wafers under the microscope

10. Tungsten sputtering:

- load wafers into Bell jar
- draw vacuum better than 10⁻⁶ torr
- refill with argon to 8 mtorr
- sputter etch wafer at 100 W for 30 second
- presputter target at 100 W for 1 minute

- sputter tungsten at 100 W for 5 minutes
(it forms approx. 25 nm tungsten)
- 15 minute cool down

11. Furnace annealing (to form tungsten silicide):

- furnace temperature 800 C
- load wafers on boat in N₂ flow
- switch to pure H₂ (2 liter/min.) and let it burn
- 5 minute warm up, 1 minute push in
- 10 minute annealing, 30 second pull out
- 5 minute cool down, switch back to N₂
- 10 minute purge before removing wafers

12. Tungsten etch (to remove unreacted tungsten from the SiO₂):

- etch wafers in Caro's acid (400 ml H₂SO₄, 20 ml H₂O₂) at 110 C
until tungsten is removed (approx. 3-5 minute)
- 10 minute rinse in DI water, blow dry with N₂
- inspect under microscope

13. Al Deposition (to form front contact):

- place wafers onto evaporator plate

- load wafer into Bell jar, draw vacuum better than 10^{-6} torr
- deposit 1 micron of aluminum at 15 A/sec.
- release vacuum, unload and inspect wafers

14. Photolithography (to define metal contact):

- 30 minute bake at 200 C
- spin negative photoresist on front
- 20 minute bake at 85 C
- align mask and expose (3 sec.)
- develop, dry in alcohol
- 30 minute post bake at 130 C
- etch Al in concentrated phosphoric acid (H_3PO_4) at 60 C
for approx. 1 minute 15 second (the presence of WSi_2 speeds up
the reaction)
- 10 minute rinse in DI water, blow dry with N_2
- remove photoresist in J-100 at 110 C
- 30 minute DI water rinse, blow dry

15. Al Deposition (to form back contact):

- same as 13. except load wafers back surface up

16. Sintering (to obtain good ohmic contact):

- furnace temperature 450 C, gas flow N₂ (2 l/min.)
- 5 minute warm up, 30 second push in
- 15 minute annealing
- 30 second pull out, 5 minute cool, unload
- ready for electrical measurements

END

2	8	H	1	0	H	8	5
---	---	---	---	---	---	---	---

FIN