CONF-941144--119

Note: This is a preprint of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the author(s).

To be submitted to 1994 Materials Research Society Fall Meeting, Boston, MA, (Vol. 373, Symposium A, *Beam-Solid Interactions for Materials Synthesis and Characterization*, ed. by D. E. Luzzi, M. Iwaki, T. F. Heinz, and D. C. Jacobson.)

Suppression of Self-Interstitials in Silicon During Ion Implantation via in-situ Photoexcitation

J. Ravi, Y. Erokhin, K. Christensen, and G. A. Rozgonyi
North Carolina State University
Raleigh, NC

B. K. Patnaik
University of North Carolina
Chapel Hill, NC

C. W. White
Oak Ridge National Laboratory
Oak Ridge, TN

Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

February 1995

Suppression of Self-Interstitials in Silicon During Ion Implantation via *in-situ* Photoexcitation

J. Ravi, Yu. Erokhin, K. Christensen, and G. A. Rozgonyi
Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695-7916

B. K. Patnaik
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC

C. W. White
Solid State Division, Oak Ridge National Labs, Oak Ridge, TN

ABSTRACT

The influence of in-situ photoexcitation during low temperature implantation on self-interstitial agglomeration following annaealing has been investigated using transmission electron microscopy (TEM). A reduction in the level of as-implanted damage determined by RBS and TEM occurs athermally during 150 keV self-ion implantation. The damage reduction following a 300°C anneal suggests that it is mostly divacancy related. Subsequent thermal annealing at 800°C resulted in the formation of {311} rod like defects or dislocation loops for samples *with* and *without* in-situ photoexcitation, respectively. Estimation of the number of self-interstitials bound by these defects in the sample *without* in-situ photoexcitation corresponds to the implanted dose; whereas for the in-situ photoexcitation sample a suppression of ≈2 orders in magnitude is found. The kinetics of the athermal annealing process are discussed within the framework of either a recombination enhanced defect reaction mechanism, or a charge state enhanced defect migration and Coulomb interaction.

INTRODUCTION

Ion implantation processing is extensively used in the fabrication of integrated circuits. In silicon, with device dimensions approaching that of the defect interaction volume, it is critical that the introduction and the redistribution of defects be controlled. The suppression of defects generated during the implantation process would enable lower thermal budgets to be used with post-implantation annealing. However, the presence of point defects[1] have been identified as the source of a phenomenon called transient enhanced diffusion (TED), known to give rise to an anamolous diffusion of dopants. We are particularly interested in defect reactions in silicon which depend upon the electronic state of the host crystal[2]. For example, perturbation of the silicon electronic sub-system by ionizing actions such as injection of minority charge carriers or light illumination, can influence the defect formation kinetics. This process has been explored by several investigators during implantation[3-5] as well as during post implantation thermal annealing[6-8]. In this investigation we demonstrate the feasibility of in-situ optical perturbation during Si^+ implantation for suppression of radiation damage at low temperatures, and show that large reductions in self-interstitial agglomeration, measured using transmission electron microscopy, occurs during subsequent high temperature annealing.

EXPERIMENTAL

Implantation into n-type (100) CZ silicon (10-20 Ω-cm) by $^{30}Si^+$ ions at an energy of 150 keV and dose of $1x10^{14}$ cm^{-2}, was performed at 45° to the sample surface. Samples were heat sunk during implantation with a silver-based paste applied between the sample and its holder, which was held at liquid nitrogen temperature. An external UV light source provided in-situ

To be published in the MRS Proc. Vol. **373** (1995)

generation of non-equilibrium charge carriers. A Hg arc lamp illuminated the sample through a quartz window yielding a power density of 700 mW/cm^2 at the wafer surface. Samples *with* (called hν) and *without* (called Ref) in-situ illumination, mounted as shown schematically in Fig.1, were simultaneously implanted and their temperature monitored with a thermocouple. Samples were subsequently examined at room temperature with Rutherford Backscattering Spectrometry (RBS)/channeling along <100> and with cross-sectional transmission electron microscopy (XTEM). The kinetics of the damage relaxation process to form dislocations was examined by subjecting the samples to an isochronal annealing in a vacuum furnace at 300, 500 and 800°C for 30 minutes.

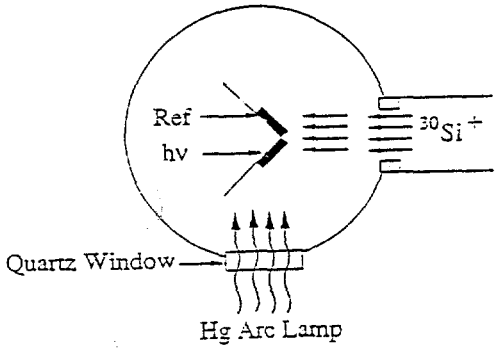

Fig.1 Plan view schematic of the experimental setup

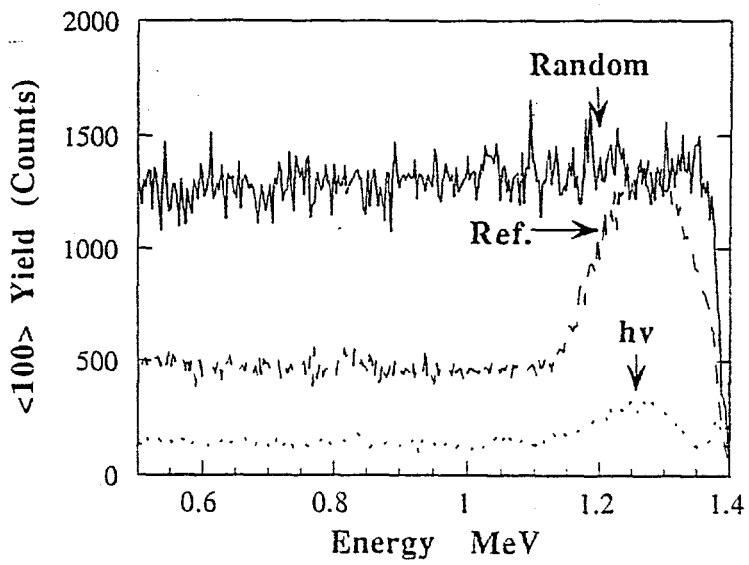

Fig.2 RBS/channeling spectra of as-implanted damage for the Ref and hν samples

RESULTS AND DISCUSSION

RBS channeling spectra obtained at room temperature of the hν and Ref samples are shown in Fig.2. The in-situ illumination produces a dramatic suppression of ion implantation damage when compared with the reference sample. Estimating the amount of suppression by determining the integrated area under each of the damage peaks, reveals ≈ 5-fold decrease in the total damage due to an in-situ illumination. In order to determine the rate of damage suppression, R*, for the data in Fig. 2 it is necessary to understand the interaction between the dominant defects within the irradiated volume. Hence, we put forth a simplified damage growth model[9] which describes the Ref and hν data. Accumulation of implantation induced damage may be described as follows:

$$\frac{dN_{i,v}}{dt} = G - kN_iN_v \qquad (1)$$

where G is the defect generation rate, N_i and N_V are the concentration of vacancies (V) and interstitials (I), respectively, and k is the kinetic coefficient of the vacancy and interstitial reaction V + I = 0 which results in damage removal. For the reference sample we assume k=0. For the sample with in-situ hν during implantation, a change in the Si electronic subsystem (point defect charge state) changes the vacancy-interstitial interaction and yields an instantaneous decrease in the damage. Solving equation (1) for the data shown in Fig.2, we obtained a value of $5*10^{-26}$ cm^3/s for k. The damage suppression rate (R*) is given by R*=kρ, where ρ is the atomic concentration. Thus, R* was found to be $3.0x10^{-3}$ s^{-1}.

Since the illumination process itself leads to a measured increase in the hν sample temperature to ≈177K, an additional experiment was run in order to separate the electronic enhancement effect from the possibility of a heating effect. We found that the implantation damage produced in a

sample resistively heated to ≈ 208K was still ≈ 1.5 times higher than the damage produced in the hν sample[10]. Therefore, the reduced damage level in the hν sample is primarily attributed to electronic and not thermal effects because the residual damage in silicon is constatnt up to implantation temperatures of 200K[11]. However, it was shown by Elliman et al[12] that the interstitial concentration determined quantitatively from the size and density of extended defects is independent of the thermal and defect histories of the sample. Therefore, a thermally activated suppression of primary damage will not necessarily reduce the observed self-interstitial agglomeration in the extended defects, leaving open the possibility that an athermal effect is responsible for suppression of the self-interstitials concentration, as demonstrated below.

The influence of in-situ illumination on near-surface damage was also evaluated using cross-sectional TEM, as shown in Figs. 3a and 3b for the Ref and hν samples, respectively. These images present a strong qualitative correlation with the RBS damage peaks in Fig. 2. An additional

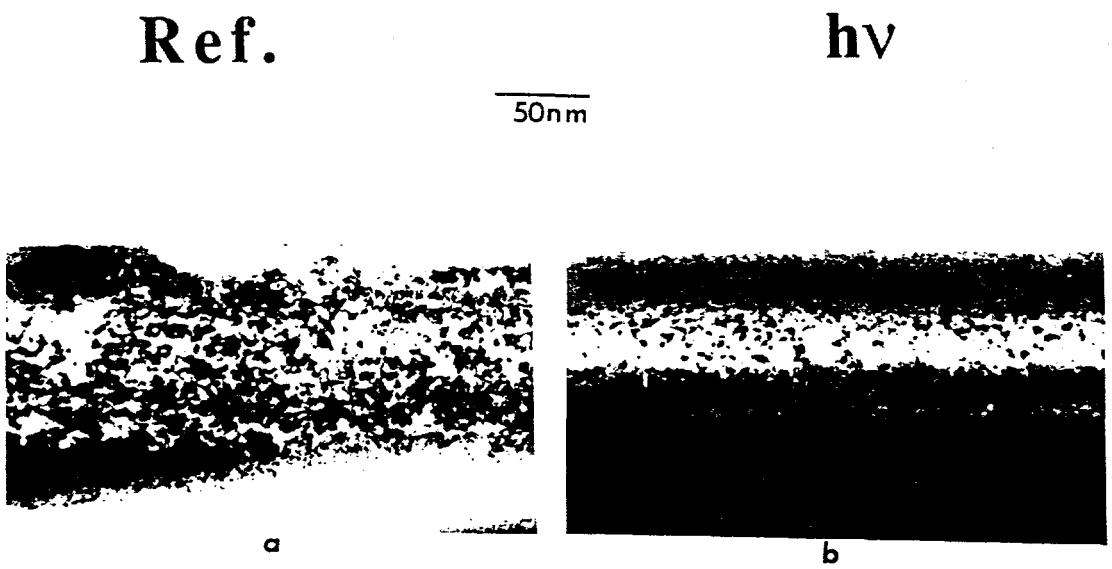

Fig. 3 X-TEM images of the as-implanted damage (150keV; $1x10^{14}cm^{-2}$; LN_2) for the a) Ref andb) hν samples

high resolution lattice image is presented in Fig.4 and indicates that amorphous areas are embedded in a predominantly crystalline host lattice, in agreement with previous investigators[9]. The density of the amorphous areas increased with depth from the surface and peaked at the projected range. Microdiffraction patterns (not shown here) were taken at three different depths from the surface with a 14 nm probe size. Evidence of a crystalline phase is present, even within the heaviest damaged region in Fig. 3, indicating a relatively small volume fraction of amorphous to crystalline phase. Qualitatively, it is seen from these images that in-situ illumination leads to a suppression of implantation damage at temperatures where no thermal annealing is known to occur[11]. Comparison of Figs. 3 a and b reveals a striking difference in damage morphology above and below Rp in the Ref and hν samples.

Isochronal annealing was performed at 300, 500 and 800°C for 30 minutes in a vacuum furnace. RBS channeling spectra for the 300°C anneal, see Fig. 5, shows a significant annealing of the damage in the hν sample ($\chi_{min} \approx 8\%$) as compared to the Ref sample, where only near-surface damage (≈200Å) has annealed out. This was also confirmed by both cross-sectional TEM and plan view TEM (not shown here) for the same samples. Since divacancies in silicon anneal out at temperatures below 300°C[13], it is likely that most of the damage in the hν sample may be constituted of divacancies. We note that in the Ref sample the annealing was only from the near surface, which is more likely to contain divacancies, as reported by Holland et. al.[9]. Annealing at 500°C produces the RBS channeling spectra of Fig. 6, where both Ref. and hν samples approach

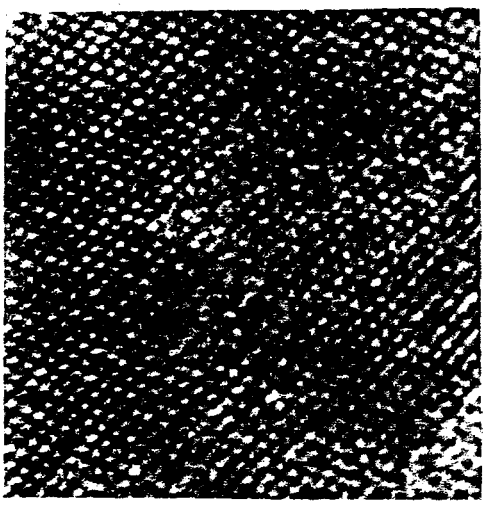

Fig. 4 High resolution lattice image of the damaged region in the Ref sample.

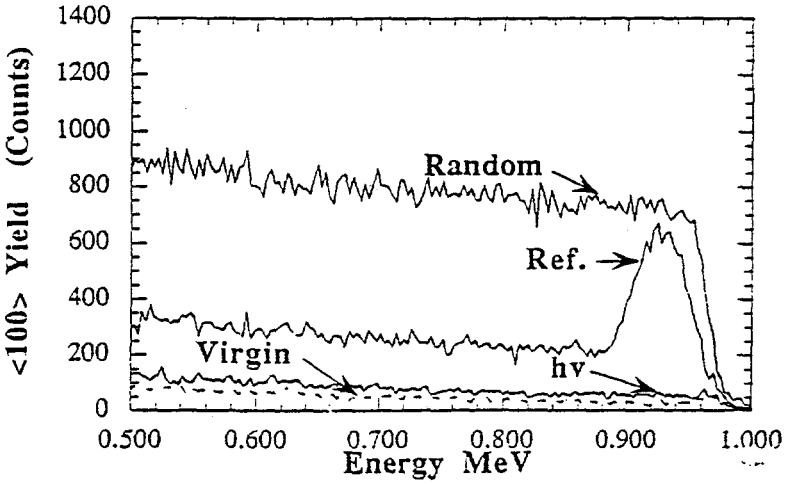

Fig.5 RBS/channeling spectra of the 300°C annealed damage for the Ref and hv samples.

that of the virgin crystal, suggesting annealing of more complex crystalline damage in the samples. Thus, the annealing data clearly implies that the in-situ photoexcitation process not only suppresses the total damage, but also the formation of higher order complexes. Upon further annealing at 800°C, shown in the plan view TEM of Fig. 7, the defects in the Ref sample were seen to be mainly in the form of loops, whereas the hv sample exhibited rod like defects. These rod like defects consist of interstitials precipitating on the {311} plane. The total number of interstitials bound to these defects were determined from the TEM measurements[14]. Interstitial densities for the Ref and hv samples were found to be $\approx 1 \times 10^{14}$ cm^{-2} and $\approx 1 \times 10^{12}$ cm^{-2}, respectively. Thus, an agreement with the "+1" model[15] is seen for our Ref sample, consistent with several recent investigators[14-16]. Since our hv samples exhibit a suppression of the self-interstitials of ≈2 orders in magnitude, it is evident that the process of in-situ photoexcitation during ion implantation effectively suppresses the presence of self-interstitials. It was recently shown in a quantitative manner by Eaglesham et al[17] that the dissolution of {311} defects creates a source of interstitials which in turn are the driving force behind transient enhanced diffusion. Thus, the hv reduction of

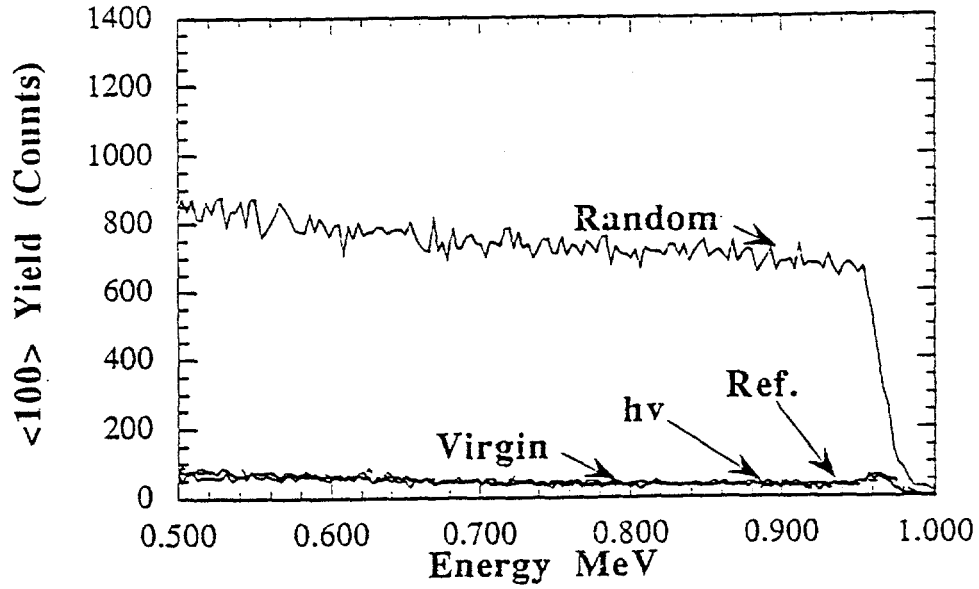

Fig. 6 RBS/channeling spectra of the 500°C annealed damage for the Ref and hv samples

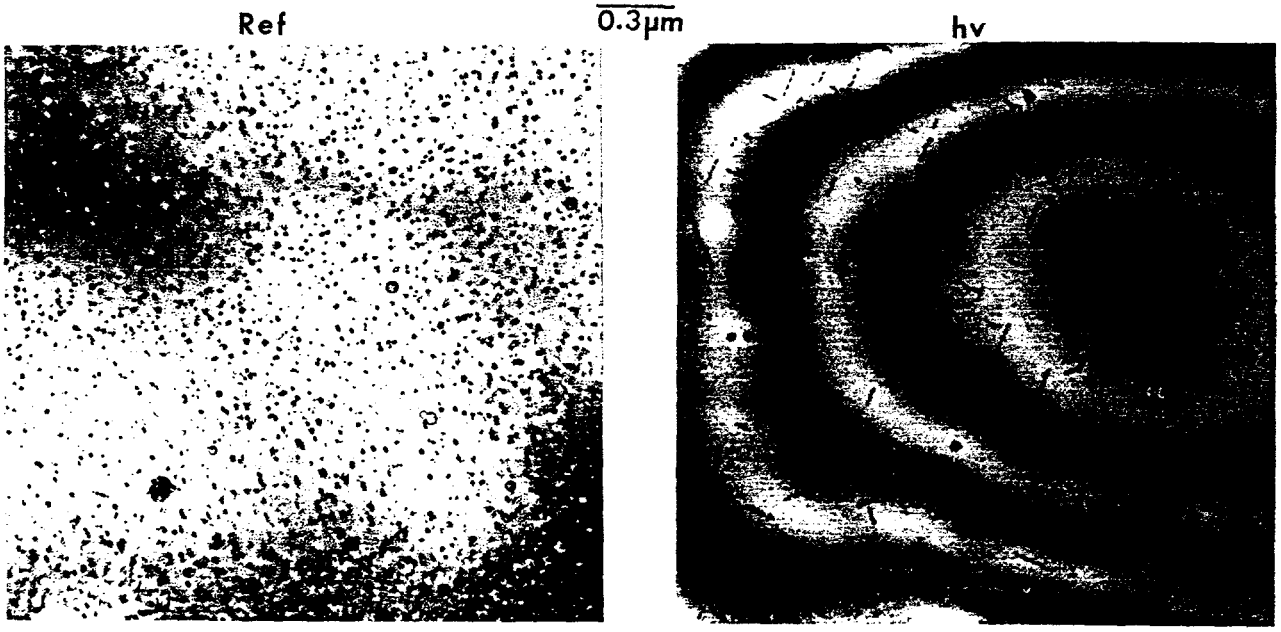

Fig. 7 Plan view images of the 800°C annealed Ref and hv samples

{311} defects is expected to produce a reduced TED. We note that Stolk, et al[16] achieved a reduced TED by introducing substitutional carbon. It is possible in our own investigation that the in-situ photoexcitation process may also enhance the interaction between residual carbon and silicon interstitials.

Under the influence of in-situ illumination two mechanisms are considered to explain the above observations. First, a change in defect charge state may be stimulated by capturing non-equilibrium charge carriers. This would lead to an increased vacancy migration[18] and enhance the Coulomb interaction between vacancies and interstitials. A second possible mechanism that may be operative, either independently or in association with the charge state effect, is recombination enhanced defect reaction (REDR). REDR has been proposed by several investigators[6,7] as a mechanism for lowering the annealing temperatures of stable defect complexes which are subjected to injection of charge carriers during the thermal annealing process. In this mechanism, the defect annealing reaction rate increases due to the local deposition of vibrational energy (a consequence of non-radiative recombination at the defect site), thereby producing a lowering of the activation barrier for defect migration and reaction. The reaction rate due to the electronic enhancement can be represented by the expression[2]:

$$R_E = \frac{\eta R_r}{N_j} \exp\{-(E_t - E_r)/kT\} \qquad (2)$$

where R_E is the rate of recombination enhanced reaction, η is the effective fraction of the recombination events which contribute to the defect reaction, R_r is the recombination rate, E_t is the reaction barrier, E_r is the recombination energy, N_j is the number of jumps required for long range migration recovery, k is the Boltzmann's constant and T is the temperature of the process. For the case when $E_r > E_t$, the reaction kinetics are athermal and therefore equation (2) reduces to:

$$R_E = \frac{\eta R_r}{N_j} \qquad (3)$$

The recombination rate R_r can be estimated by $R_r = \sigma v G \tau$, where σ is the capture cross-section, v is the carrier thermal velocity, G is the carrier generation rate and τ is the life time of the carriers in an ion implanted sample. It was recently shown by us[10] that the REDR may be a reasonable option for the defect migration and reactions at such low temperatures.

CONCLUSIONS

In summary, we have demonstrated that *in-situ* illumination during Si^+ implantation leads to a significant suppression of radiation damage at temperatures where thermal effects are not operative. In-situ photoexcitation suppresses the primary damage, as well as the formation of higher order vacancy complexes, leading to a lower thermal stability. A reduction in interstitial density by ≈2 orders of magnitude upon annealing at 800°C was found for the hν sample, whereas in the Ref sample it correlated with the implanted dose. REDR may be the responsible mechanism for the observed in-situ defect suppression. However, the operation of other mechanisms such as a change in charge state leading to an enhanced defect migration or favorable Coulomb interaction between vacancies and interstitials cannot be excluded.

ACKNOWLEDGEMENTS

Financial support for this work from the National Science Foundation (DMR-9215538) is gratefully acknowledged. Research at the Oak Ridge National Laboratory was sponsored by the Division of Materials Science, U.S. Department of Energy, under contract DE-AC05-840RZ1400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. P. M. Fahey, P. B. Griffin and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).
2. L.C. Kimerling, Solid State Electronics **21**, 1391 (1978).
3. H.J. Stein, Appl. Phys. Lett. **2**, 235 (1963).
4. V.N. Mordkovich, A.B. Danilin, Yu. Erokhin, S.N. Boldyrev, MRS Proc. **201**, 477 (1991).
5. Yu. Erokhin, J. Ravi, C. W. White and G. A. Rozgonyi, Nucl. Instr. Methods **B**, in press (1995).
6. J. Krynicki and J.C. Bourgoin, Inst. Phys. Conf. Ser. No. **46**, 482 (1979).
7. M.T. Asom, J.L. Benton, R. Sauer, L.C. Kimerling, Appl. Phys. Lett. **51**, 256 (1987).
8. K Wada, H. Nakanishi and K. Yamada, Appl. Phys. Lett. **63**, 2525, (1993).
9. O. W. Holland, C. W. White, M. K. El-Ghor, and J. D. Budai, J. Appl. Phys. **68**, 2081, (1990)
10. J. Ravi, Yu. Erokhin, K. Christensen, G. A. Rozgonyi, B. K. Patnaik and C. W. White, to be published in Appl. Phys. Lett. (1995).
11. S. M. Sze, VLSI Technology, McGraw Hill, pg. 240 (1983)
12. R. G. Elliman and I. V. Mitchell, to be published, Proc of the Mat. Res. Soc., **373**, (1995).
13. J. Ravi, Yu. Erokhin, S. Koveshnikov, G. A. Rozgonyi and C. W. White, Proc. Mat. Res. Soc. **316**, 104, (1994)
14. M. Seibt, J. Imschweiler and H.-A. Hefner, in ECS Proc. Vol 94-10 (SanFransico 1994), pp. 720.
15. K. S. Jones, S. Prussin and E. R. Weber, Appl. Phys. **A45**, 1, (1988).
16. P. A. Stolk, H.-J. Gossmann, D. J. Eaglesham, D. C. Jacobson, H. S. Luftman and J. M. Poate, to be published, Mat. Res. Soc. Proc. **354**,(1995)
17. D. J. Eaglesham, P. A. Stolk, H.-J. Gossmann, and J. M. Poate, Appl. Phys. Lett. **65**(18), 31, (1994)
18. J.C. Bourgoin and J.W. Corbett, J. of Chem. Phys. **59**, 4042 (1973).