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MODIFICATION OF ELECTRONIC MATERIALS WITH MeV IONS(1)

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Résumé

Les faisceaux d'ions d'énergie autour du MeV permettent souvent des opportunités uniques pour la modification des propriétés électroniques des matériaux. J'en présente ici 3 exemples provenant de notre récent travail. Le premier est la production de couches SiO_2 profondément enterrées dans du Si par implantation d'oxygène. Le matériau résultant a été caractérisé par XTEM. Le second implique la modification de InP par implantation de N et GaAs par O implantation. Dans ces cas nous avons utilisé XTEM, analyse RX, canalisation d'ions et des réactions nucléaires de profil pour étudier l'endommagement de structure et son comportement par recuit thermique. Le troisième exemple montre comment la résistivité de film mince de carbone amorphe peut être changée par un facteur allant jusqu'à 10^4 par bombardement d'ions. Le mécanisme de ce phénomène est étroitement lié à celui proposé pour la désorption par ion MeV.

Abstract - MeV ion beams often allow unique opportunities for the modification of the electronic properties of materials. In this talk I shall discuss three such examples from our recent work. The first is the production of deeply buried SiO_2 layers formed in Si by MeV oxygen implantation for a variety of implantation and annealing conditions. The resulting material has been characterized by XTEM. The second involves the modification of InP by N implantation and GaAs by O implantation. In these cases we have used XTEM, x-ray rocking curve analysis, ion channeling, and nuclear reaction profiling to study the structural damage and its behavior under thermal annealing. The third example shows how the resistivity of thin amorphous carbon films can be changed over a range of 10^4 by MeV ion bombardment. The mechanism for this phenomenon is shown to be closely related to that proposed for MeV ion induced desorption.

1. INTRODUCTION

When one talks about the possible use of MeV ions in materials modification it is legitimate to question whether there is sufficient justification in the uniqueness of the outcome to overcome the greater cost involved. Obviously, even in the most optimistic projections the modification of electronic materials will mainly continue to involve lower cost techniques like diffusion, keV-ion implantation, and liquid-phase and molecular-beam epitaxy. There are, however, several areas where MeV ions offer decided advantages; in this paper I shall describe several that my group at Caltech has explored.

The most obvious advantage that one sees in MeV-ion implantation is the greater range of the ions, which allows them to be implanted deeper into a material or through overlying layers. This advantage can be exploited in two common situations: minimizing the damage at the surface, so that one can subsequently grow high quality epitaxial layers of other materials on the surface with less difficulty; and the need to make transverse modifications deep in complex structures layered in the vertical direction. In both cases one is exploiting the lower collisional damage produced by the incident ions when they enter the material. The first three examples that I shall cover provide variations on this general theme.

In my fourth example, the fact that the loss of energy to the target material is mainly by electronic interactions is exploited to produce modifications that are very different than those obtained through keV-ion bombardment. In this situation one arrives at a unique product that is capable of an enormous range of variability.

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2. FORMATION OF SiO_2 BY MeV OXYGEN IMPLANTATION IN Si

In order to control the region in which current can flow in semiconductor devices, it is desirable to create electrically isolated regions within the structure. In silicon much attention has been given to creating a semiconductor-on-insulator (SOI) structure that can be used for this purpose and as a substrate for further steps in the fabrication process. In this respect a method called separation by implanted oxygen (SIMOX) has become important. /1/ It requires a high fluence keV oxygen ion implantation followed by high temperature annealing. For example, a stoichiometric SiO_2 layer is formed under 200 keV oxygen implantation at fluences above 1.4×10^{18} cm $^{-2}$ followed by annealing at 1300°C. /2/

We have chosen to look at higher energy implantations under a variety of implantation and annealing conditions. /3/ The bombardments were performed using an EN tandem to accelerate 2 and 5 MeV oxygen ions for fluences between 10^{15} and $2x10^{18}$ cm^{-2}; the current densities were 3-8mA/cm^2. The substrate temperatures were -196°C, room temperature, and 500°C - although beam heating probably caused the target surface to be significantly hotter. Annealing was done in evacuated quartz tubes at an oxygen partial pressure less than 10^{-6} Torr.

The samples were subsequently thinned and studied by conventional TEM and HREM with a Phillips EM 430 electron microscope operating at 300 kV. EELS was performed with a Gatan 607 Electron Energy Loss Spectrometer installed on the same microscope operating at 200kV.

Although the heaviest damage occurs in the region where the ions stop, there is considerable damage at shallower depths as well. Several strategies have been involved in the implantation; for example, keeping the substrate hot causes the oxygen to diffuse into the region where it reacts to form SiO_2. /4/ We have found, however, that by keeping the target cold during implantation the oxygen concentration is kept high until annealing can both produce an amorphous SiO_2 layer and at the same time anneal the damage in the overlying layers.

Figure 1 compares XTEM micrographs of samples implanted with 5 MeV ions to fluences of $2x10^{18}$ cm^{-2} at room temperature and at liquid nitrogen temperature. In both cases a 900 nm SiO_2 layer is formed, but the low temperature case has an order of magnitude lower threading dislocation density and smaller silicon inclusions in the SiO_2 layer. In both cases the SiO_2 layer surface is well defined, and the surface of the silicon is high quality crystalline material that is suitable for further processing. Overall, the samples implanted at low temperature are superior and the technique seems extremely promising.

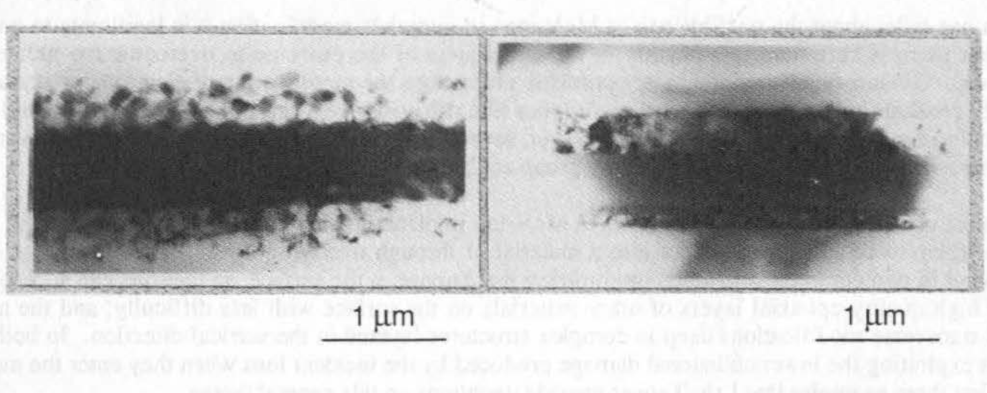


Fig. 1. XTEM micrographs of samples implanted with $2x10^{18}$cm^{-2} 5 MeV oxygen ions at (left) room temperature, and (right) low temperature, after annealing at 1300°C.

3. FORMATION OF BURIED HIGH RESISTIVITY LAYERS IN InP BY N IMPLANTATION

InP is of considerable interest for the fabrication of microwave and opto-electronic devices because of the high mobility that can be obtained in n-type InP and the emission wavelength of the InGaAsP/InP system, which is in the right range for fiber communication. It has, however, not been easy to produce insulating layers in the III-V materials by implantation. For example, proton implantation requires a high dose but only yields a resistivity of 10^3 ohm-cm. /5/ Low energy Fe implantation into n-type InP has given a 10^6 ohm-cm resistivity; for this process Fe-doping during the growth of bulk semi-insulating InP crystals is employed. /6/ This technique has been used to make channeled substrate buried heterostructure lasers. /7/

We have also produced 10^6 ohm-cm layers in n-type InP crystals by nitrogen ion implantation. /8/ This has been achieved for 5 MeV nitrogen ions at a beam current of $1 mA/cm^2$ for fluences between $5x10^{14}$ and 10^{16} cm^{-2}. Implantation was followed by studies of annealing behavior; high resistivity layers were formed by processing at 500°C for 20 minutes, but even much longer, higher temperature annealing (e.g., 650°C for 60 minutes) produced no degregation of the effect. /8/

All of these device-oriented results rest on a solid foundation of detailed characterization that cover a very wide range of implantation and annealing conditions. /9, 10/ Examples are shown in the figures below. Figure 2 shows the strain (as measured by the x-ray rocking curve technique) induced in InP crystals by nitrogen implantation. In Fig. 3 are the channeling RBS spectra which show how the annealing process improves the crystal quality in the region near the surface of the example.

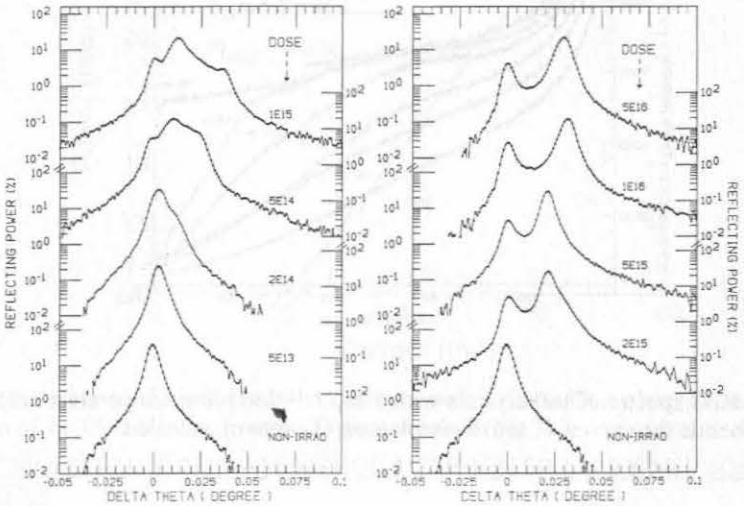
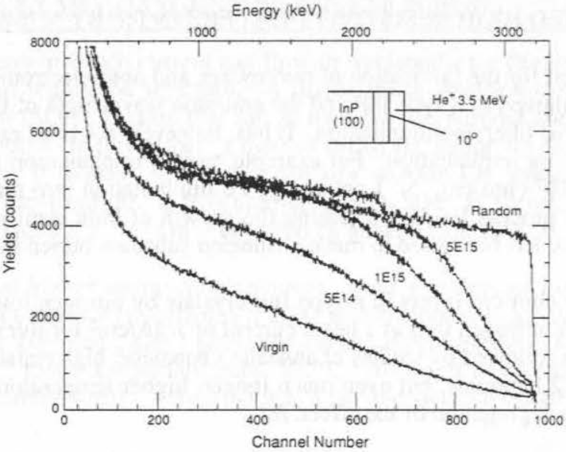


Fig. 2. X-ray rocking curves of the 5 MeV-^{15}N-ion implanted InP (400) symmetrical diffraction with respect to the InP(100) substrate. The radiation-induced strain and the strain saturation are shown. (These samples have not been annealed.)

In addition to these techniques, we have used TEM to study the growth of the amorphous, high resistivity layer with ion fluence and the recovery of crystallinity in the overlying material by annealing. The use of nuclear reaction profiling with the $^{15}N(p,\alpha\gamma)^{12}C$ reaction established the location of the implanted nitrogen and confirmed that the nitrogen did not diffuse during the annealing. This result shows that the nitrogen is bound chemically and not just trapped in the radiation damaged region caused by the implantation.



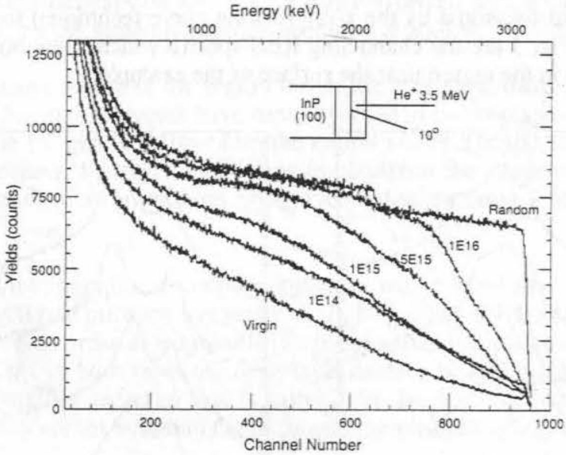


Fig. 3. Channeling RBS spectra of InP crystals with 5 MeV ^{15}N at room temperature with a sequence of fluences as marked beside the curves, (1 top) as-implanted, (1 bottom) annealed.

4. HIGH EFFICIENCY GRINSCH LASERS MADE BY MeV-O IMPLANTATION

As in the case of InP, we have devoted a major effort to studying the damage produced by MeV ion implantation in GaAs in order to produce deeply buried, high resistivity layers. /11,12/ On the left side of Fig. 4 one sees the complexity of a transverse modification of a GRINSCH laser (i.e., the regions labeled "Burying Layer") that is required to provide the boundaries of the GaAs wave guide region. Removing the original material in these regions physically and re-growing the doped material is a difficult and expensive process and typically give an overall conversion efficiency (electrical to optical power) of less than 50% and a breakdown voltage of approximately 5V.

On the right side one sees the implanted regions produced using a suitable mask on top of the contact to define the active GaAs region. For the device shown we used 1.8 MeV oxygen ions at a fluence of $2x10^{15}$ cm^{-2}. The device was then annealed at 650°C to remove the damage produced by the implantation.

The resulting device produced a laser with a low threshold current of 21mA and an efficiency of 85%, which is the highest value ever reported. The breakdown voltage was 30V. /13/ The power versus current curve is shown in Fig. 5.

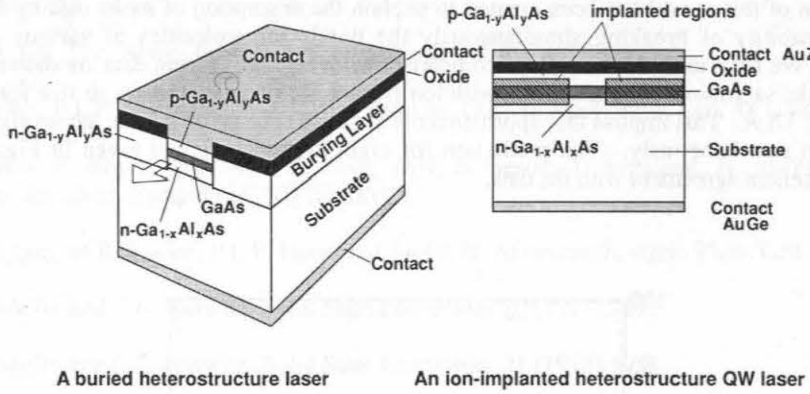


Fig. 4. A schematic diagram of the GRINSCH laser described in the text.

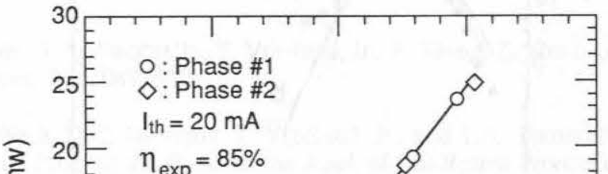


Fig. 5. Threshold and transmission efficiency of quantum well AlGaAs/GaAs laser fabricated with MeV-O-ion implantation of $2\times10^{15}/cm^2$. (Schematic diagram shown in Fig. 4.)

5. RESISTIVITY MODIFICATION IN AMORPHOUS CARBON FILMS BY MeV-ION BOMBARDMENT

In previous work we have shown that MeV ion irradiation of amorphous carbon films produces a change in their conductivity. /14/ For low energy (keV) heavy ions the conductivity is reduced; for high energy ions (MeV) the conductivity increases. The full range of conductivity that can be covered is 10^4; the portion of that range of variability achievable by either type of irradiation alone obviously depends on the original state of the film. This change in conductivity was interpreted as resulting from the creation of small highly conducting graphite crystals in the poorly conducting amorphous carbon by the electronic interaction with the MeV ions, which increases the conductivity; the break up of such crystals by low energy bombardment reverses the effect.

The dependence of the conductivity change on ion energy (as shown in Fig. 6 below and Fig. 2 of /14/) peaks more sharply and at a lower energy than the energy loss, dE/dx, of the ion in the film. An explanation for this behavior is that the shower of secondary electrons generated along the ion's path can simultaneously break a number of adjacent chemical bonds in the material, allowing the lower energy state (graphite) to be achieved. /14/ This idea is a version of the model proposed for the destruction of living cells by ionizing radiation. /15/ Since at higher bombarding energies the energy density associated with the secondary electrons drops because of their longer ranges, the effect peaks at a lower energy than dE/dx and decreases more quickly.

A recent version of this model has been created to explain the desorption of molecules by MeV ions, in which the probability of breaking simultaneously the bonds for molecules of various sizes can be estimated. /16/ We have used this model for comparison with our most recent data, as shown in Figure 6. /17/ By using the saturation of conductivity with ion fluence we deduce an average size for the graphite crystals created, 3.8 Å. This implies that approximately six atoms are involved, i.e., about eight bonds that must be broken simultaneously. The prediction for eight broken bonds is given in Fig. 6, which is obviously in excellent agreement with the data.

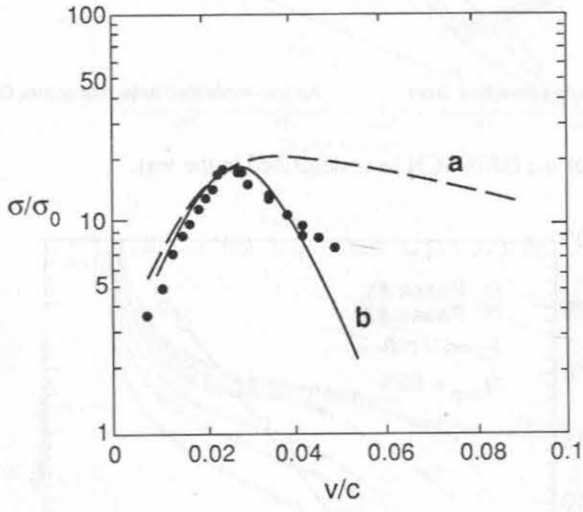


Fig. 6. The conductivity (in units of its initial value) of an originally amorphous carbon film as a function of the velocity (in units of c) for bombarding ^{35}Cl ions. The ion fluence at each point was taken at the mid-point (logarithmic) of the total change in conductivity with ion fluence. The solid curve (b) is the fit given by the model of /16/ where eight carbon-carbon bonds are broken simultaneously by the secondary electrons generated by the ion's passage. The dashed curve (a) is dE/dx for ^{35}Cl ions in carbon. (The data were taken from /17/.)

6. CONCLUSIONS

The first three examples show that there are applications in semiconductor device fabrication where the implantation of MeV ions can play a unique role. Although the ion fluences required for SiO_2 isolation-layer formation in silicon are sufficiently high (>10^{18} cm^{-2}) that very long implantations are required, the formation of similar layers in GaAs and InP can be accomplished at much more modest fluences (~10^{15} cm^{-2}). Thus, for the III-V semiconductors there appears to be ready application of the technique - especially for the transverse modifications required in solid-state laser fabrication.

In the case of the resistivity modification of amorphous carbon films, one now has a technique that allows conductivity changes over a broad range. Such conductivity variations can be written with extremely high spatial resolution to create controlled patterns in an intrinsically high resistivity medium. It is, of course, of practical interest to determine whether keV electron beams or short wavelength lasers can replace the MeV ions that we have employed here.

REFERENCES

/1/ See Mat. Res. Soc. Symp. Proc. Vol. 53(1986) and Vol. 107 (1988).

/2/ G.K. Cellar, P.L.F. Hemment, W.K. West, and J.M. Gibson, Appl. Phys. Lett. 48 (1986) 532.

/3/ C.W. Nieh, F. Xiong, C.C. Ahn, Z. Zhou, D.N. Jamieson, T. Vreeland, Jr., B. Fultz, and T.A. Tombrello, Mat. Res. Soc. Symp. Proc. 107 (1988) 73.

/4/ C.G. Tuppen, M.R. Taylor, P.L.F. Hemment, and R.D. Arrowsmith, Appl. Phys. Lett. 45 (1984) 57.

/5/ J.P. Donnelly and C.E. Hurwitz, Solid State Electronics 20 (1977) 727.

/6/ J.P. Donnelly and C.E. Hurwitz, Solid State Electronics 21 (1978) 475.

/7/ D.P. Wilt, B. Schwartz, B. Tell, E.D. Beebe, and R. Nilson, Appl. Phys. Lett. 44 (1984) 290.

/8/ F. Xiong, T.A. Tombrello, T.R. Chen, H. Wang, Y.H. Zhuang, and A. Yariv, Nucl. Instr. Meth. B (1989) in press.

/9/ C.R. Wie, T. Jones, T.A. Tombrello, T. Vreeland, Jr., F. Xiong, Z. Zhou, G. Burns, and F.H. Dacol, Mat. Res. Soc. Symp. Proc. 74 (1987) 517.

/10/ F. Xiong, C.W. Nieh, D.N. Jamieson, T. Vreeland, Jr., and T.A. Tombrello, Mat. Res. Soc. Symp. Proc. 100 (1988) 105 and Proc. of the Conf. on the Appl. of Ion Beams Produced by Small Accelerators, Jinan, PRC (1987) in press.

/11/ C.R. Wie, T. Vreeland, and T.A. Tombrello, Nucl. Instr. Meth. B16 (1986) 44; Phys. Rev. B33 (1986) 4083; J. Appl. Phys. 59 (1986)3743.

/12/ T.T. Bardin, J.G. Pronko, F.A. Junga, W.A. Opyd, A.J. Mardinly, F. Xiong, and T.A. Tombrello, Nucl. Instr. Meth. B24/25 (21987) 548.

/13/ F. Xiong, T.A. Tombrello, H. Wang, T.R. Chen, H. Morkoç, and A. Yariv, submitted to the fall meeting of the Mat. Res. Soc., Nov. 1988.

/14/ As discussed in T.A. Tombrello, Nucl. Instr. Meth. B/24/25 (1987) 517.

/15/ E.J. Kobetich and R. Katz, Phys. Rev. 170 (1968) 391 and R. Katz, Nucl. Track Detection 2 (1978) 1.

/16/ A. Hedin, P. Håkansson, B. Sundqvist, and R.E. Johnson, Phys. Rev. B31 (1985) 1780.

/17/ T. Jones, Ph.D. thesis in Appl. Phys., Caltech (1989) in preparation.