



ELSEVIER



Viscosity of amorphous InP during room temperature structural relaxation

L. Cliche^{a,*}, S. Roorda^a, R.A. Masut^b

^a *Groupe de recherche en physique et technologie des couches minces, Département de Physique, Université de Montréal, C.P. 6128 succ. centre-ville, Montréal, Québec, H3C 3J7, Canada*

^b *Groupe de recherche en physique et technologie des couches minces, Département de Génie Physique, École polytechnique de Montréal, C.P. 6079 succ. centre-ville, Montréal, Québec, H3C 3A7, Canada*

Abstract

The shear viscosity η of amorphous InP has been determined during structural relaxation at room temperature. Following amorphization by ion implantation, the in-plane and out-of-plane deformation have been measured by surface profilometry. The structural relaxation consists of a volume expansion which is partly accommodated by shear plastic flow. It was deduced from the in-plane and out-of-plane deformation, that η increases linearly with time with an initial η_0 value of $(9 \pm 4) \times 10^{15}$ Ns/m² and a slope $\dot{\eta} = (4.8 \pm 0.4) \times 10^{10}$ N/m².

1. Introduction

Structural relaxation [1] is a phenomenon that occurs in all amorphous solids, including amorphous Si [2] and amorphous InP [3] prepared by ion implantation. In a-Si, structural relaxation has been likened to annealing of point defects in crystalline Si, in view of similarities in the kinetics and temperature dependencies of these processes [2]. It is not unlikely that a similar analogy between structural relaxation and defect annealing holds in other solids.

Very few point defects in amorphous solids have been identified directly (examples are the dangling bond [4] and the Sb-vacancy complex [5] in a-Si). However, defect populations can be probed indirectly, for example by heat release [2] or viscosity measurements [6,7]. In this contribution, we present measurements of the evolution of the in-plane and out-of-plane deformation of a-InP layers created by ion implantation into c-InP. A slow, persistent structural relaxation at room temperature is observed [3]. This structural relaxation consists of a volume expansion which is partly accommodated by shear plastic flow. Quantitative analysis of the time evolution of the strains allows us to determine the viscosity of the a-InP as a function of time over several months.

2. Experimental details

Semi-insulating InP(100) wafers were degreased and clamped to a copper block, using vacuum grease for improved thermal contact. They were then implanted at room temperature with 10^{14} cm⁻² Se ions at several energies (see Table 1), with low beam current, limiting the areal power density to less than 0.6 W/cm². Alternating stripes of amorphous/crystalline InP were produced by using a steel contact mask placed directly on the sample. The implantations were carried out in a vacuum of 1×10^{-7} mbar or better. Raman spectroscopy was used to verify that InP is indeed amorphous after 2 MeV, 10^{14} cm⁻² Se implantation.

After implantation, the surface was profiled with a stylus profilometer (Dektak 3030ST). Each surface profile of 8 mm of the masked surface covered 10 periods of alternating amorphous/crystalline material. We repeated these measurements several times over a period of about 70 days following implantation. Successive profiles were taken at the same place on the samples and with the same applied stylus force (0.05 mN). The c-InP/a-InP step was measured on surface profiles from which we have subtracted the curvature and each reported value is the average of twenty individual steps with the error being the standard deviation. The radius of curvature was also obtained from the surface profile. Curvatures are considered positive when the sample is bent away from the implanted surface.

* Corresponding author.

Table 1
Ion implantation parameters and amorphous layer thickness

Sample #	Implantation energies [MeV]	total Se fluence [10^{14} cm^{-2}]	d [μm]
1	2, 3.6, 6, 10, 17, 24, 30	7	8.0 ± 0.5
2	2, 3.6, 6, 10, 17	5	5.4 ± 0.3
3	2, 3.6, 6, 10	4	4.2 ± 0.4
4	2, 3.6, 6	3	3.1 ± 0.2
5	2, 3.6	2	2.3 ± 0.2

Some unmasked samples were chemically beveled in a solution of bromine:methanol (1:19). The bevels were made deep enough to reach the substrate under the amorphized layer. Again with a profilometer, we measured the thickness of the amorphous layer by measuring the depth of the bevel at the amorphous/crystalline interface (they are reported in Table 1).

3. Results and discussion

3.1. Surface profiles

Surface profile measurements of an InP sample (#1) before and after implantation are presented in Fig. 1. The surface profile of the InP substrate before implantation (top curve) is smooth and has a small initial positive curvature ($R = 32.5 \text{ m}$). Immediately after implantation (middle curve), the curvature of the sample has increased ($R = 6.3 \text{ m}$) and there is a depression of the surface at all the implanted regions. Eleven days after the implantation (bottom curve), the curvature of the sample is even larger ($R = 4.3 \text{ m}$) while the depression of the implanted surface has diminished. The depression of the implanted surface indicates a density change (compaction) of the amorphous material. With the low fluence needed to amorphize the material ($7 \times 10^{14} \text{ ions/cm}^2$ at most), both the added material and the estimated amount of sputtered material are negligible. Therefore, the step height is a direct measure of the out-of-plane deformation.

For this particular InP sample with its top $8 \pm 0.5 \mu\text{m}$ thick amorphized layer, the averaged step height immediately after amorphization was determined to be $45 \pm 2 \text{ nm}$ which gives an out-of-plane strain of $\epsilon_{\text{out}} = -0.56 \pm 0.02\%$. The decrease of the radius of curvature implies an increase of the in-plane strain ϵ_{in} . In order to elastically relieve the stress associated with the in-plane deformation, the wafer bends by an amount that is determined by the balance of forces and moments between the underlying wafer and the implanted region. The bottom curve shows that after the implantation, when the sample is left at room temperature, the strain ϵ_{in} continues to increase while the out-of-plane strain ϵ_{out} becomes less negative. These changes are discussed in Sections 3.3 and 3.4.

3.2. Hammering

A depression of the implanted surfaces suggests that there is a compaction of the implanted material. However, we observe a positive curvature which indicates a compressive in-plane stress while compacted material should be in tensile stress (i.e. curved in the opposite direction). At the end of the implantation, the out-of-plane dimension of the a-InP region has decreased while its in-plane dimensions have increased. A possible explanation for such a deformation would be the hammering effect which has been observed in a variety of amorphous materials subjected to MeV ion bombardment [8]. This is not the subject of this presentation and will be discussed elsewhere.

3.3. Room temperature structural relaxation

Fig. 2 shows the variation of the step height (Fig. 2a) together with the evolution of the curvature of the sample (Fig. 2b) over periods of up to 10 weeks, for five different samples. The solid lines were drawn for ease of viewing. The step height decreases with time and appears to saturate after several months. Simultaneously, the curvature increases, which corresponds to the buildup of compressive in-plane stress. Both these changes are indicative of an overall expansion of the a-InP starting after the implantation. The decrease of the step height indicates expansion in the out-of-plane direction. At the same time, the expansion pushes in the in-plane direction which leads to the increased curvature. In the following section, the in-plane and out-of-plane strains will be evaluated quantitatively, which allows the determination of the viscosity of the a-InP.

3.4. Viscosity of amorphized InP

The average out-of-plane strain due to the relaxation $\epsilon_{\text{out}}^{\text{relax}}$ is given by the change in step height, relative to that

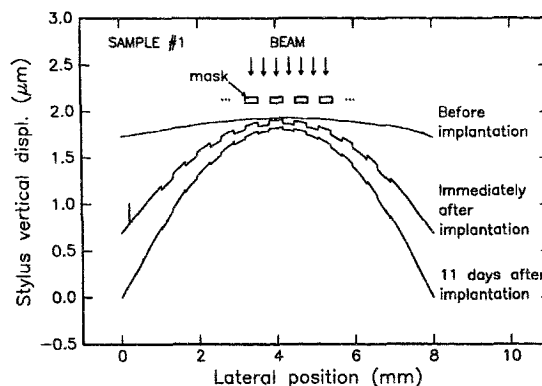


Fig. 1. Surface profile of an InP sample prior to the implantation (top curve), immediately after implantation through a mask (middle curve), and 11 days after implantation (bottom curve).

at $t = 0$, immediately after the ion implantation, divided by the amorphous layer thickness. The average in-plane strain due to relaxation, ϵ_{in}^{relax} , can be calculated from the integrated biaxial stress σ in the film which is given by the Stoney formula [9]:

$$\sigma - \sigma_0 = \frac{E_s t_s^2}{6(1 - \nu_s) t_f R} - \sigma_0 = \frac{E_f \epsilon_{in}^{relax}}{(1 - \nu_s)}, \quad (1)$$

where E_s and E_f are the Young modulus of the substrate and the film respectively, t_s and t_f , the thickness of the substrate and the film, ν_s , the Poisson ratio of the undamaged InP and R , the radius of curvature of the substrate. σ_0 is the initial stress. Comparing ϵ_{in}^{relax} and ϵ_{out}^{relax} with the change in strain due to density changes $\epsilon_p = \Delta\rho/3\rho$,

we find that $\epsilon_{out}^{relax} > \epsilon_p + 2\nu_f \epsilon_{in}^{relax}/(1 - \nu)$. This indicates that some of the overall expansion is accommodated by flow. The strain associated with flow, ϵ_{pl} , can be related to ϵ_{in} and ϵ_{out} according to [10]:

$$\epsilon_{out} = \frac{1 + \nu_f}{1 - \nu_f} \epsilon_{in} + 3\epsilon_{pl}, \quad (2)$$

where ν_f is the Poisson ratio of the film (taken to be equal to ν_s), and we have dropped the superscript relax. If we assume Newtonian viscous flow, ϵ_{pl} obeys the following differential equation [10]:

$$\dot{\epsilon}_{pl} = \frac{E_f \epsilon_{in}}{6(1 - \nu_f)\eta}, \quad (3)$$

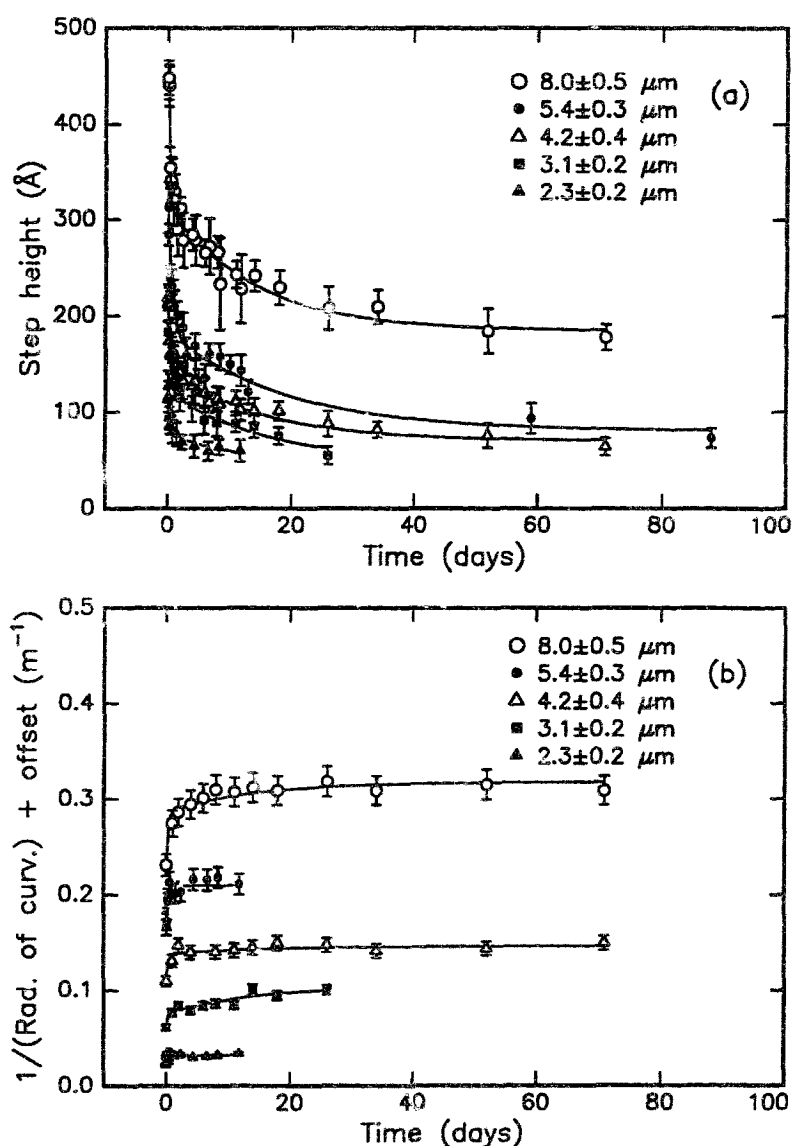


Fig. 2. Time evolution of (a) step height and (b) curvature, for five different samples.

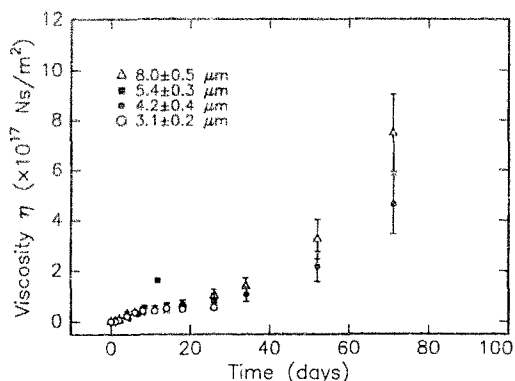


Fig. 3. Room temperature viscosity of ion amorphized InP as a function of relaxation time for four different samples.

where η is the instantaneous shear viscosity of the amorphous relaxing film. The curvature measurements and the step height permit us to calculate ϵ_{in} and ϵ_{out} respectively. From the in- and out-of-plane strain, ϵ_{pl} was evaluated according to Eq. (2). We took $E_s = 6 \times 10^{10}$ N/m 2 , the Young modulus of crystalline InP in the $\langle 001 \rangle$ direction and assumed that $E_s = E_t$. Once ϵ_{pl} is known, the shear viscosity η of a-InP as a function of time follows from Eq. (3).

Fig. 3 shows the evolution of the viscosity for four different samples. The four sets of points overlap in spite of the differences in film thickness. This should be the case, since the viscosity is a property of the material, which does not depend on sample geometry. Immediately after implantation, $\eta = (9 \pm 4) \times 10^{15}$ Ns/m 2 (which is comparable to the viscosity of a-Si at 200°C [6]) and it is seen to increase roughly linearly with a slope of $(4.8 \pm 0.4) \times 10^{10}$ N/m 2 .

It has been argued that the viscosity of amorphous solids is inversely proportional to the concentration of defects contributing to flow (e.g. Ref. [6]). A linear increase in η would then correspond with a bi-molecular decay of the defect population. The present data show some deviations from a strictly linear behaviour. It is at this point not clear whether these deviations are random or systematic.

4. Conclusion

In conclusion, we have used surface profilometry to measure the in-plane and out-of-plane strain of InP following amorphization by high energy ion bombardment. A persistent, room temperature structural relaxation has been observed which manifests itself as an overall expansion and an increase in the shear viscosity η . The expansion is partly accommodated by shear plastic flow, which becomes progressively more difficult as the viscosity increases. The initial value of η is $(9 \pm 4) \times 10^{15}$ Ns/m 2 and it increases roughly linearly with a slope of $(4.8 \pm 0.4) \times 10^{10}$ N/m 2 .

Acknowledgments

It is a pleasure to acknowledge the expert assistance of P. Bérichon and R. Gosselin with the operation of the tandem accelerator, R. Arès who set up the bevel preparation technique, and M. Verhaegen who did some of the profilometry. This work is financially supported by the Natural Science and Engineering Research Council of Canada (NSERC) and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR).

References

- [1] G.W. Scherer, *Relaxation in Glass and Composites*, (Wiley, New York, 1986).
- [2] S. Roorda, W.C. Sinke, J.M. Poate, D.C. Jacobson, S. Dierker, B.S. Dennis, D.J. Eaglesham, F. Spaepen, and P. Fuoss, *Phys. Rev. B* 44 (1991) 3702.
- [3] L. Cliche, S. Roorda and R. Masut, *Appl. Phys. Lett.* 65 (1994) 1754.
- [4] P.A. Thomas, M.H. Brodsky, D. Kaplan and D. Lepine, *Phys. Rev. B* 18 (1978) 3059.
- [5] G.N. van den Hoven, Z.N. Liang, L. Niesen and J.S. Custer, *Phys. Rev. Lett.* 68 (1992) 3714.
- [6] A. Witvrouw and F. Spaepen, in: *Kinetics of Phase Transformations*, eds. M.O. Thompson, M.J. Aziz and G.B. Stephenson, MRS Symp. Proc. vol. 205 (Materials Research Society, Pittsburgh, 1992) p. 21.
- [7] C.A. Volkert, *J. Appl. Phys.* 74 (1993) 7107.
- [8] S. Klaumünzer, M. Rammensee, S. Löffler and H.C. Neitzert, *J. Mater. Res.* 6 (1991) 2109.
- [9] P.A. Flinn, D.S. Gardner and W.D. Nix, *IEEE Trans. Elect. Dev.* ED-34 (1987) 689.
- [10] C.A. Volkert, *J. Appl. Phys.* 70 (1991) 3521.