

Nanoindentation of Ion Implanted and Deposited Amorphous Silicon

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ABSTRACT

The deformation behavior of both ion-implanted and deposited amorphous Si (a-Si) films has been studied using spherical nanoindentation, followed by analysis using Raman spectroscopy and cross-sectional transmission electron microscopy (XTEM). Indentation was carried out on both unannealed a-Si films (the so-called unrelaxed state) and in ion implanted films that were annealed to 450°C to fully relax the amorphous film. The dominant mode of deformation in unrelaxed films was via plastic flow of the amorphous phase rather than phase transformation, with measured hardness being typically 75-85% of that of crystalline Si. In contrast, deformation via phase transformation was clearly observed in the relaxed state of ion implanted a-Si, with the load-unload curves displaying characteristic discontinuities and Raman and XTEM indicating the presence of high-pressure crystalline phases Si-III and Si-XII following pressure release. In such cases the measured hardness was within 5% of that of the crystalline phase.

INTRODUCTION

It is well known that diamond cubic Si-I undergoes a series of pressure-induced phase transformations during mechanical loading using both diamond anvil and indentation apparatus. It has been shown that Si-I first transforms to a metallic β -Sn (Si-II) phase during loading at a pressure of ~11 GPa [1-5]. During pressure release, the material undergoes further transformation to crystalline phases (Si-III and Si-XII) and, during fast unloading in indentation experiments, can transform to an a-Si phase [3].

For a-Si, early indentation measurements on ion-implanted amorphous films showed that the mechanical deformation appeared to depend on the preparation conditions or the "state" of the amorphous phase [6]. The so-called relaxed a-Si state [7] (in which the implanted amorphous layer is annealed to ~450 °C prior to indentation) exhibited very similar load-unload indentation curves to those of crystalline Si, including a similar hardness. However, unannealed (or unrelaxed) a-Si appeared to deform plastically at lower loads and exhibit a somewhat lower hardness. The more recent indentation measurements of Follstaedt *et al.* [8] confirmed that the hardness of relaxed ion implanted a-Si approached that of Si-I but that unrelaxed a-Si was slightly softer. Our very recent measurements [9] on ion implanted a-Si have shown that the relaxed state undergoes phase transformations under indentation whereas the unrelaxed state appears to flow plastically. In this paper, we extend such measurements to compare the indentation behaviour of both ion implanted and CVD-deposited amorphous Si.

EXPERIMENTAL DETAILS

In this current study continuous layers of a-Si were prepared by one of two methods: by ion-implantation of (100) Si-I wafers [9] and by PECVD deposition of a-Si on (100) Si-I. The

PECVD-deposited a-Si was pre-annealed for 5 min at a temperature of ~ 300 °C in a nitrogen atmosphere but this treatment is insufficient to relax the film [7,10]. The typical a-Si film thicknesses were between 600 and 900 nm. Portions of the deposited and ion-implanted samples were annealed for 30 min at a temperature of ~ 450 °C in an argon atmosphere to attempt to fully relax the layers [10] but not induce any crystallization.

A series of indentations were then performed on both deposited and ion-implanted (in each case on unannealed and annealed) a-Si samples using an Ultra-Micro-Indentation-System 2000 with spherical indenters of ~ 5.0 and 2 μm radii at room temperature. For the case of the 2 μm radius indenter, the penetration depth at maximum applied load (20 mN) for the thinnest films was less than one third of the a-Si film thickness and, hence, the underlying substrate is expected to have a minimal affect on the deformation behavior of the film.

After indentation, Raman spectra were recorded with a Renishaw 2000 Raman Imaging Microscope using the 632.8 nm excitation line of a helium-neon laser and a beam spot of ~ 1.0 μm radius. Residual indent impressions were prepared for cross-sectional transmission electron microscopy (XTEM) using a FEI XP200 focused ion beam system [4] and samples were analysed in a Philips CM 300 operating at an accelerating voltage of 300 kV.

RESULTS AND DISCUSSION

Figure 1(a) shows a load versus penetration plot of unrelaxed ion-implanted a-Si loaded to 50 mN. No discontinuities on either the loading or unloading sections of the curve are observed. In contrast, the nanoindentation curve taken from relaxed ion-implanted a-Si, as shown in figure 1(b), exhibits a clear discontinuity on unloading. Such an event is typically referred to as a “pop-out” event [5] and is indicative of phase transformations in Si [5,11]. Furthermore, a discontinuity on loading with a spherical indenter (called “pop-in”) can be observed with crystalline Si but this is not easily observed when indenting relaxed a-Si.

Figure 2 displays the Raman spectra of indents in relaxed and unrelaxed ion-implanted amorphous silicon and of pristine amorphous silicon, all spectra showing clearly the broad a-Si peak at around 470 cm^{-1} . In the unrelaxed case no evidence for phase transformations could be found but for the spectrum of the relaxed sample we observed Raman shifts indicating the presence of Si-III at 383 cm^{-1} and 435 cm^{-1} and indicating Si-XII at 351 cm^{-1} and 396 cm^{-1} .

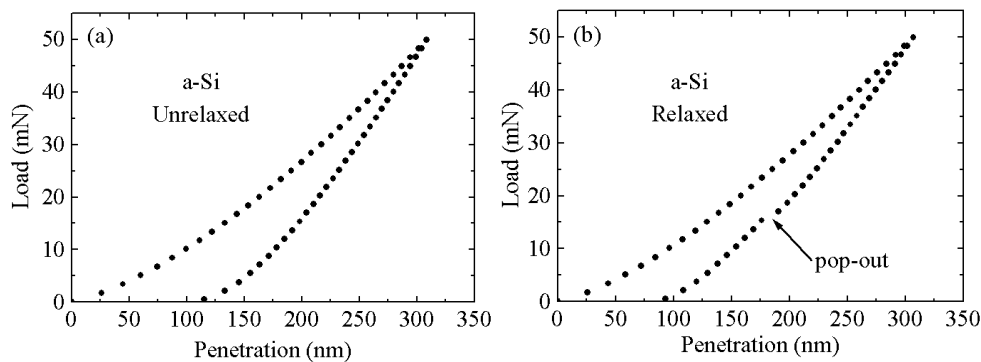


Figure 1. Load-unload curves of (a) unrelaxed and (b) relaxed 900 nm thick ion-implanted a-Si films using a continuous load cycle with a spherical indenter of ~ 5 μm radius.

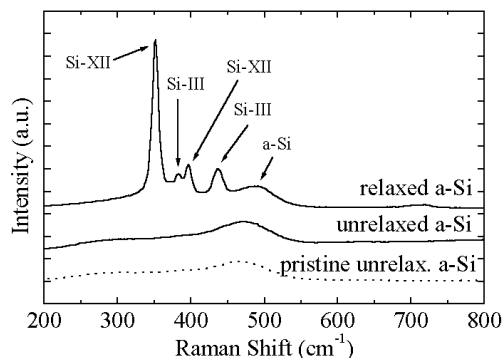


Figure 2. Raman spectra of pristine unrelaxed *a*-Si and spectra from indentations in relaxed and unrelaxed *a*-Si. Indentations made to a 50 mN load in 650 nm thick, ion-implanted *a*-Si with a continuous load–unload cycle using a spherical indenter of ~ 5 μm radius.

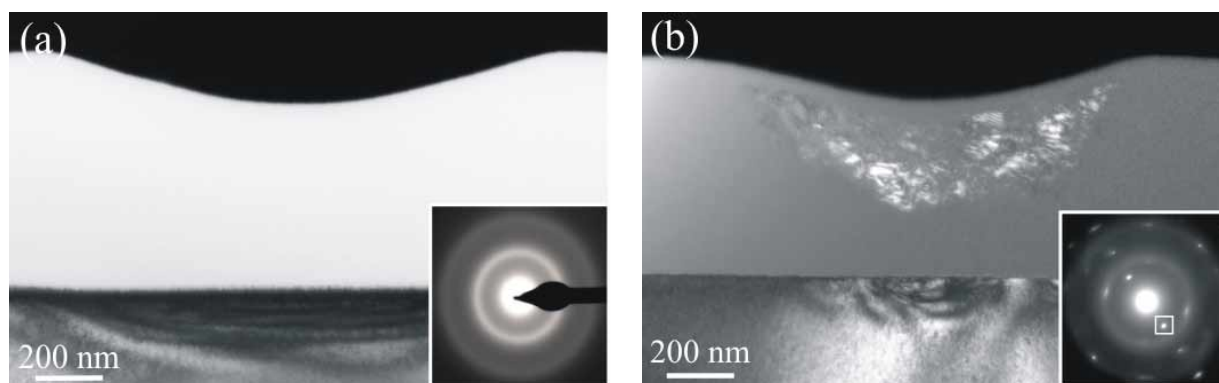


Figure 3. (a) BF XTEM image of an indent in unrelaxed 600–650 nm thick ion-implanted amorphous silicon; (b) DF XTEM image of an indent in relaxed 600–650 nm thick, ion-implanted amorphous silicon, the diffraction spot used to form the DF image is marked with a box in the inset. All indents were made using a continuous load cycle with a ~ 2 μm radius indenter to a maximum load of 20 mN. The SADPs were taken from the region directly under the residual indent impressions.

Figure 3(a) shows a XTEM bright-field image of a 20 mN indent in unrelaxed ion-implanted *a*-Si made using a ~ 2.0 μm radius indenter. A selected area diffraction pattern (SADP) of the region immediately beneath the residual indent shows only the diffuse rings characteristic of an amorphous structure. In contrast, the dark-field (DF) image of a residual indent in relaxed ion-implanted *a*-Si, shown in figure 3(b), illustrates very clearly that phase transformations have occurred during loading and unloading. The DF image was taken using the boxed diffraction spot from Si-III/Si-XII shown in the inset to this figure. These extra diffraction spots arise from Si-III/XII.

The above behavior clearly indicates that phase transformations from an amorphous state to a crystalline state can occur at room temperature under indentation in relaxed *a*-Si. As indicated elsewhere [9], we can interpret the difference in the mechanical behavior of relaxed and unrelaxed films in terms of the different bonding configurations in these states: relaxed *a*-Si has near-fully-coordinated Si in a continuous random network, whereas unrelaxed *a*-Si contains a

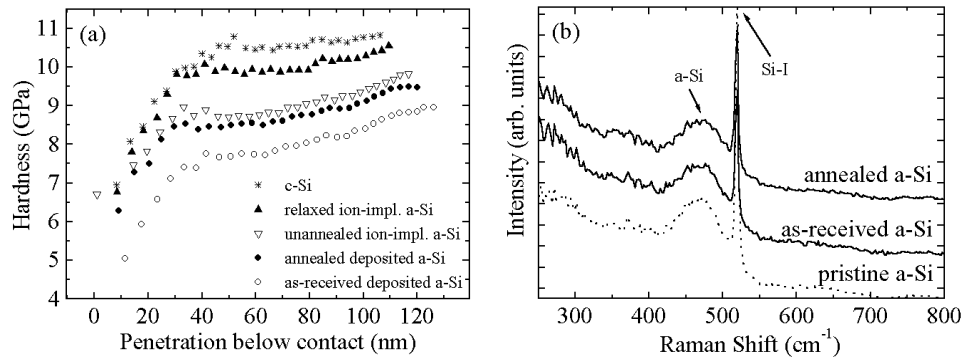


Figure 4. (a) Hardness of c-Si, compared with relaxed and unrelaxed ion-implanted and deposited a-Si films. The hardness data was taken for loading to 25 mN using a partial load-unload cycle for ~ 5 μm radius spherical indenter. (b) Raman spectra of pristine Si and spectra from indentation to a maximum load of 50 mN in 900 nm thick, deposited a-Si with a continuous load-unload cycle using a spherical indenter of ~ 5 μm radius.

high density of dangling bonds. In the latter case, the dangling bonds may aid plastic flow of the material.

The load-unload curves for deposited a-Si were almost identical to those in figure 1(a) for unrelaxed ion implanted a-Si, indicating that no phase transformation had taken place in this case. A comparison of the hardness data for each of the film cases is illuminating. Figure 4(a) shows the hardness (as a function of penetration depth) of annealed and unannealed, ion-implanted and also deposited a-Si, compared with that of crystalline Si-I. Clearly, relaxed ion-implanted a-Si is nearly as hard as Si-I (within 5%). However, the other films are considerably softer. Note that we have annealed the deposited a-Si film to 450 °C for 30 minutes in an attempt to relax the film but, although its hardness increases slightly, the material does not undergo transformation. We do not understand this behavior but suggest that the deposited films could differ from relaxed (annealed) ion implanted films in a number of respects: they may contain a significant impurity content (including hydrogen) and could exhibit porosity. As a result, the annealed deposited film may depart from the near-fully-coordinated relaxed ion implanted film and this could enhance their ability to deform plastically under indentation. We intend to further investigate this issue. The lack of phase transformation in the deposited films is confirmed by Raman analysis. Figure 4(b) shows Raman spectra of indents in as received and annealed deposited a-Si, compared with pristine deposited a-Si prior to indentation. No evidence for a phase transformation is observed, with peaks from Si-I as well as from the amorphous layer being visible. However, we would not expect Si-I peaks to be observed for 900 nm thick films and believe that pinholes may be the reason for their observation. If this is the case, then it may reinforce structural differences between the annealed ion implanted and deposited a-Si films.

CONCLUSION

In conclusion we have observed an amorphous to crystalline phase transformation at room temperature in relaxed (annealed) ion implanted a-Si during indentation, resulting in the end phases Si-III and Si-XII following unloading. Phase transformations are not the primary mode of deformation with deposited a-Si films or with unannealed (unrelaxed) ion implanted films. In the latter case, these films deform via plastic flow of the film under the indenter. Whereas the

hardness values of relaxed films that undergo phase transformation are within 5% of the value for crystalline Si-I, the films that plastically deform are considerably softer, with a hardness of 75-85% of the crystalline value.

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