Effect of hydrogen on nanoindentation-induced phase transformations in amorphous silicon

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(Received 29 September 2009; accepted 2 November 2009; published online 17 December 2009)

The effect of local hydrogen concentration on nanoindentation-induced phase transformations has been investigated in ion-implanted amorphous silicon (a-Si). Elevated concentrations of H ranging from 5×10^{18} to 5×10^{20} cm^{-3}, over the depth of indentation-induced phase transformed zones have been formed in the a-Si by H ion-implantation. Indentation has been performed under conditions that result in phase transformed zones composed totally of Si-III/Si-XII in the "H-free" samples. Deformation during indentation and determination of phase transformation behavior has been examined by analysis of load/unload curves, Raman microspectroscopy, and cross-sectional transmission electron microscopy (XTEM). With increasing H content, the probability of forming Si-III/Si-XII and the volume fraction of Si-III/Si-XII decrease. XTEM shows that these reduced volumes are randomly distributed within the phase transformed zone and are surrounded by indentation-induced a-Si. For a H concentration of 5×10^{20} cm^{-3}, the probability of forming Si-III/Si-XII is reduced to 0.5 compared to 1 in "H-free" material and for those indents that exhibit the Si-III/Si-XII end phase the volume fraction is approximately 60 %. We suggest that the monohydride bonding configuration of Si and H in a-Si reduces the formation of the high pressure crystalline phases by retarding growth of the crystallites through a similar mechanism to that of hydrogen-retarded solid phase crystallization of a-Si to diamond cubic crystalline Si-I phase. © *2009 American Institute of Physics*. [doi:10.1063/1.3267853]

I. INTRODUCTION

There has been significant interest over recent years in nanoindentation-induced phase transformations in Si.[1–9] During loading, a transformation to the β-Sn phase (Si-II) occurs at a critical pressure of ~12 GPa. On unloading, the Si-II further transforms to either amorphous silicon (a-Si) or a mixture of high pressure polycrystalline phases (Si-III and Si-XII); the latter being favored for slow unloading and is usually accompanied by a pop-out event.[1,3,6,7] These phase transformations are well characterized but are still not well understood.

More recently, studies that have compared the nanoindentation-induced phase transformations in crystalline Si (c-Si) and ion-implanted (relaxed[10]) a-Si have revealed that both materials undergo similar phase transformations during loading and subsequent unloading.[7,11] On unloading, however, the high pressure crystalline phases (Si-III/XII) form much more readily during indentation in an a-Si matrix. For example, volumes of high pressure phases were formed in a-Si with unloading rates at over three orders of magnitude greater than the unload rates required to form these phases in c-Si.[7]

Recent work by the current authors on plasma enhanced chemical vapor deposited (PECVD) a-Si films found that the films do not readily undergo phase transformations on indentation loading/unloading. The reasons for this are not well understood but one possibility is that the high impurity content in the deposited films compared to a "pure" film created by ion-implantation may prevent both the ability of the a-Si to undergo phase transformations during loading and, if phase transformation does occur, the formation of the high pressure phases during unloading. In particular, O and H are found in high concentrations (10^{19}–10^{21} cm^{-3}) in PECVD deposited films compared to H levels of $\leq10^{18}$ cm^{-3} in a-Si formed by Si ion-implantation. The current authors recently investigated the effect of O on the phase transformation behavior in ion-implanted a-Si and found that at concentrations above $\sim8\times10^{19}$ cm^{-3} the formation of Si-III/Si-XII on unloading was severely inhibited.[12] The aim of the current study is to quantitatively study the effect of H while separating this from effects caused by other impurity content and variations in a-Si microstructure. This is done through ion-implantation of H into ion-implanted a-Si to controllably add a range of H concentrations into a "pure" a-Si layer over the depth range of the phase transformed zones formed by subsequent indentation. Indentation is performed under conditions that ensure the formation of Si-III/XII in the phase transformed zones for nominally "H-free" ($H<10^{18}$ cm^{-3}) ion-implanted a-Si. Analysis of the load/unload curves, Raman microspectroscopy, and cross-sectional transmission electron microscopy (XTEM) are used to study the effect of H on the phase transformation behavior.

II. EXPERIMENT

All samples were created by ion-implantation of Czochralski grown Si(100) crystalline wafers p-doped with boron to a resistivity of 10–20 Ω cm. A 2 μm thick surface

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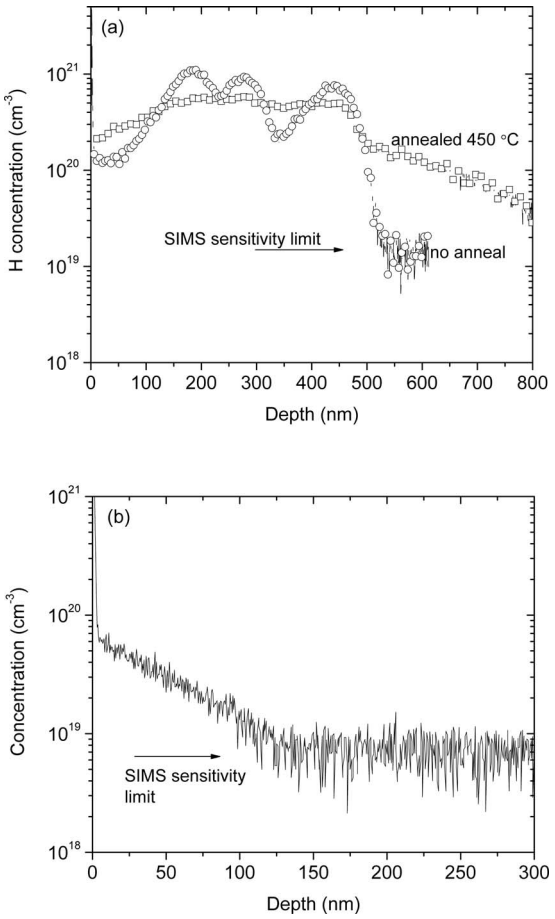

FIG. 1. (a) Shows concentration-depth profiles for as-implanted and relaxed samples implanted with H to achieve a peak concentration of $\sim 5 \times 10^{20}$ cm^{-3} extracted using secondary ion-mass spectroscopy (SIMS). The depth profile extends over the depth of the phase transformed zones ($\sim$500 nm). Following the relaxation anneal at 450 °C, the H diffuses making the concentration more constant. The sensitivity of the SIMS measurement for H is $\sim 10^{19}$ cm^{-3}. (b) shows a concentration of a H-free a-Si sample following the relaxation anneal. H in-diffuses from the sample surface increasing the very near surface H concentration. This will modify the near surface of the depth profiles for the 5×10^{18} cm^{-3} sample.

layer of a-Si was created by multiple energy implantation of Si. Samples were then cleaved and implanted with H at energies of 10, 20, and 40 keV to various fluences. Following a relaxation anneal at 450 °C for 30 min diffusion of H results in an approximately constant concentration of H over a depth range up to 500 nm below the surface (the phase transformed zones extend $\sim$500 nm below the surface). Figure 1(a) shows concentration-depth profiles of H before and after annealing at 450 °C for an implant to create a layer of a-Si(H) with a H concentration of $\sim 5 \times 10^{20}$ cm^{-3}. Three implanted samples were created with average H concentrations of $\sim 5 \times 10^{18}$, 5×10^{19}, and 5×10^{20} cm^{-3}, as well as a sample containing no additional implanted H (labeled "H-free"). Figure 1(b) shows a concentration-depth profile of H following the relaxation anneal of a "H-free" sample. Hydrogen diffuses from the sample surface during this annealing resulting in a profile with a peak surface H concentration of $\sim 6 \times 10^{19}$ cm^{-3} and decreases to the background concentration over the first 100 nm. This surface H will be present in all samples, thus modifying the first 100 nm of the H depth profile for the lower concentration samples.

Indentation was performed using an ultramicro indentation system 2000 fitted with a $\sim$4.3 μm radius spherical tip. Loading in 10 increments to 80 mN (average loading rate of 3.6 mN/s) was followed by unloading in 40 increments (average unloading rate of 0.9 mN/s). These conditions typically result (for "H-free" a-Si) in a phase transformed zone extending approximately 500 nm below the sample surface. Furthermore, it is known that high pressure crystalline phases (Si-III and Si-XII) are formed for all indents made under these conditions in "pure" ion-implanted a-Si.[7,8,11,12] A prime indicator for the formation of these phases during unloading is the presence of a pop-out on the unloading curve that corresponds to the nucleation of a large volume of Si-III/Si-XII mixed end phase. The microstructure of Si-III/XII material varies somewhat between indents made under identical conditions as a result of the nucleation and growth process. Therefore, the probability of a pop-out occurring during unloading and evidence for the formation of Si-III/XII was extracted, respectively, from analysis of the load/unload curves and Raman spectra from a series of 25 indents made in each sample.

Following the indentation tests, every residual indent was measured by Raman spectroscopy using a Renishaw 2000 instrument fitted with a HeNe laser focused to a spot of ~ 1 μm diameter. These measurements provide a method for detecting the presence of Si-III/XII and information on the approximate volume and residual stress states of Si-III/XII. The measurements can also be correlated with the load/unload curves from the indentation tests.

Finally XTEM measurements were performed on selected indents. XTEM cross-sections were fabricated using a focused ion-beam milling process which is described elsewhere.[13,14] The samples were then imaged using a Philips CM 300 transmission electron microscope.

III. RESULTS

Figure 2 shows representative load/unload curves with the various features observed during on the unloading for indents made in this study. The number of clear pop-outs observed on unloading decreases with increasing H content with a higher fraction of curves exhibiting the kinklike features. Also shown are examples of Raman spectra from unindented a-Si and an indent containing Si-III/Si-XII.

Figure 3 summarizes the Raman data and load/unload curve analyses. The probability of detecting Si-III/Si-XII, occurrence of clear pop-outs, and occurrence of *kinks* and clear pop-outs (i.e., probability of observing any feature on unloading) in the unload curve is plotted as a function of implanted H concentration. It was shown in a previous study on the effect of O on the phase transformations that the clear pop-outs can appear more *kinklike* and, at high O concentrations, can only be observed in the derivatives of the unload curves.[12] Thus, kinks are defined as features that are not always clearly observable on the unload curve but can be observed on the derivative. Raman data indicates that Si-III/Si-XII is formed in all indents for concentrations up to 5×10^{19} cm^{-3}. A pop-out or kink occurs on unloading for all indents made in these samples. For a H concentration of 5

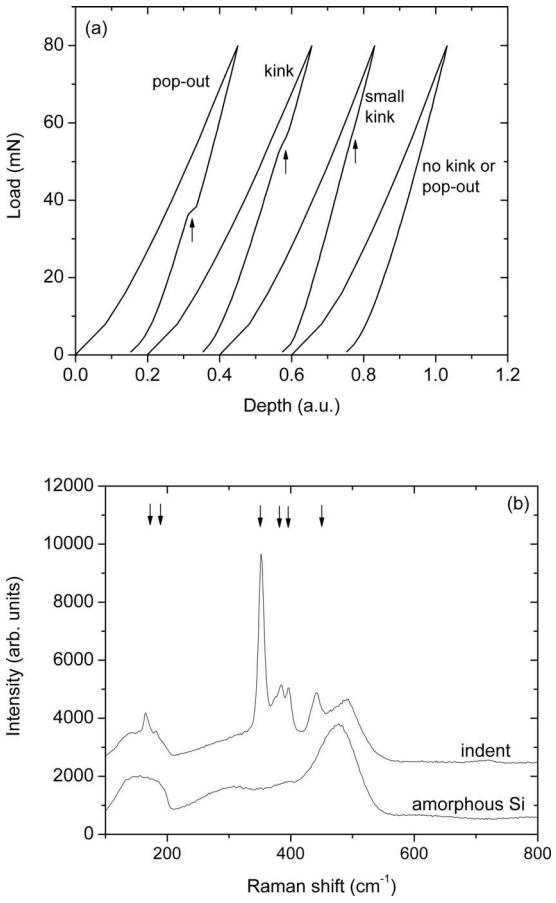

FIG. 2. Typical load/unload curves (a) observed from indentation of the a-Si containing various amounts of H. Examples of clear pop-outs, kinks, and no features on unloading are shown and labeled. The load/unload curves all have the same overall shape except for the range of features on unloading. Typical Raman spectra (b) from unindented a-Si and from an indent containing significant volumes of Si-III/Si-XII. The peaks associated with Si-III and Si-XII are labeled with arrows. The large peak at 350 cm^{-1} was used to estimate the volume of fraction of the high pressure phases. The spectra are offset for clarity.

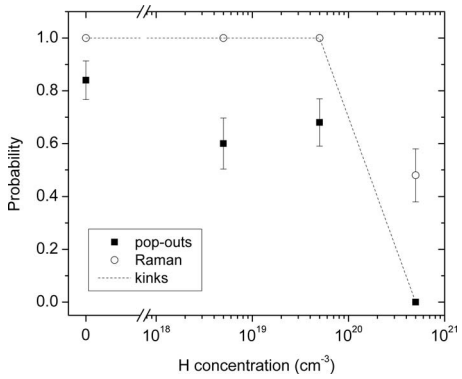

FIG. 3. Probability of observing a clear pop-out and kink (defined as only being observable in the derivative of the unload curve) during unloading as a function of local H concentration. Also shown is the probability for detecting a volume of Si-III/Si-XII in the residual indent as a function of H concentration. The probability of a pop-out decreases and is 0 for the highest H concentration. A kink is detected in all indents except for the highest H concentration sample. The probability of detecting Si-III/Si-XII in residual indents decreases from 1 to ~0.5 when the H concentration exceeds 5×10^{19} cm^{-3}.

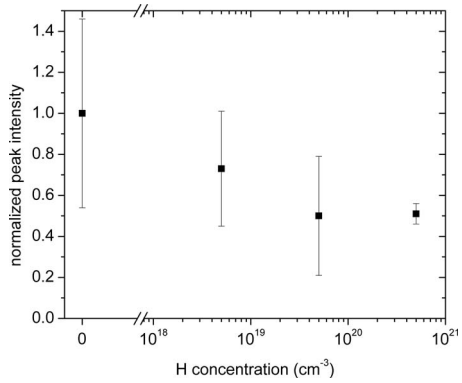

FIG. 4. Normalized intensity of the Raman peak associated with Si-XII (representative of all peaks associated with Si-XII/Si-III and therefore the volume of these phases) as a function of H concentration. This decreases with increasing H concentration and is approximately half as intense for the 5×10^{20} cm^{-2} sample as in the H-free sample.

$\times 10^{20}$ cm^{-3}, the probability of forming Si-III/Si-XII (measured by Raman) decreases to approximately 0.5. Interestingly, pop-outs/kinks associated with the formation of these phases are not observed at this concentration.

Figures 4 and 5 show further details extracted from the Raman measurements. Figure 4 shows the average intensity of the most intense Raman peak associated with the Si-III/Si-XII phases (peak at 350 cm^{-1} assigned to Si-XII—see Fig. 2). This peak intensity provides an indication of the volume of the high pressure phases in the phase transformed zone. The most intense (Si-XII) peak is used as other peaks associated with Si-III/Si-XII are substantially less intense and become barely discernable from the background signal as the volumes of these phases decrease with increasing H concentration. The volume of Si-III/Si-XII, estimated from Raman peak intensity, decreases with increasing H concentration and is approximately half that of the "H-free" sample for concentrations $\geq 5 \times 10^{19}$ cm^{-3}. Figure 5 shows the average Si-XII peak (at 350 cm^{-1}) position as a function of H concentration. The position of this peak and others (not shown here) assigned to Si-III and Si-XII (see Fig. 2) provides information on the residual stresses of the phases. Although the position varies significantly across the 25 indents

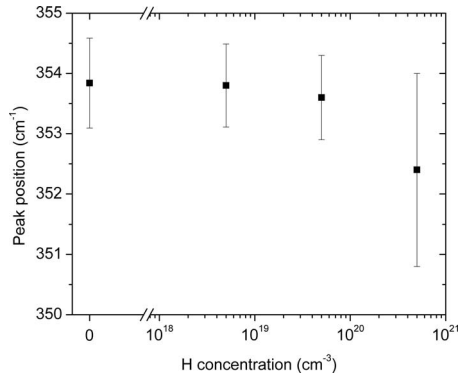

FIG. 5. Peak position of the Raman peak associated with Si-XII as a function of H content. For the highest H concentration this decreases from ~354 to ~352.5 cm^{-1}. This lower wavenumber indicates a reduction in the residual compressive stress in the residual indents. This corresponds to the reduced volumes of the Si-III/Si-XII phases formed in these indents.

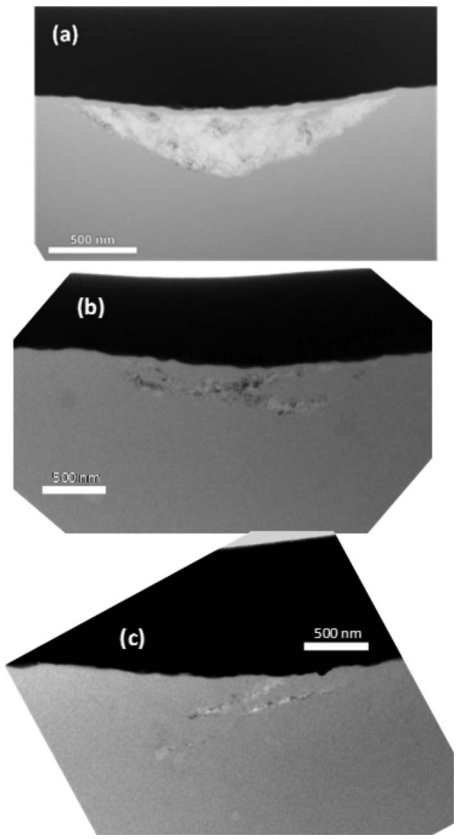

FIG. 6. XTEM images from selected residual indents. (a) Cross-section taken from an indent made in nominally H-free material (from Ref. 7). (b) An indent made in the 5×10^{19} cm^{-3} sample and (c) an indent made in the 5×10^{20} cm^{-3} sample. A reduction in volume fraction of Si-III/Si-XII compared to that in the H-free sample is clearly visible. These smaller volumes are randomly distributed within the transformed zone and are surrounded by a-Si.

per sample, the average position drops by ~1.5 wavenumbers from ~354 to ~352.5 cm^{-1} at the highest H concentration.

Figure 6 shows XTEM images of selected indents made in a H-free sample and the 5×10^{19} and 5×10^{20} cm^{-3} samples. The reduced volume of Si-III/Si-XII in each of the higher H concentration samples is clearly observed. The zones of Si-III/Si-XII are randomly distributed within the phase transformed zones and are surrounded by a-Si.

IV. DISCUSSION

The results of this indentation study show that the formation of Si-III/Si-XII on unloading is inhibited when the local H concentration exceeds $\sim5\times10^{18}$ cm^{-3}. Under the indent conditions used here the probability of forming Si-III/Si-XII decreases from 1 (for "H-free" a-Si) to ~0.5 for a H concentration of 5×10^{20} cm^{-3}. Furthermore, the average volume fraction in indents containing the high pressure phases decreases relative to the H-free samples with increasing H concentration.

Before discussing the changes in phase transformation behavior as a result of ion-implanted H concentrations, it is important to consider the effect of indiffusion of H from the Si surface during the relaxation anneal and its role on the phase transformation behavior during indentation. Following the relaxation anneal the H concentration is greater than $\sim10^{19}$ cm^{-3} at depths less than ~100 nm. Hence, H alone indiffusing from the surface during a relaxation anneal is unlikely to be responsible for the transformation of a-Si to Si-II since for the microscale indents of this and previous studies,[7,11] the phase transformed zone extends at least 500 nm below the surface which is well beyond where the concentration of H is significant. For similar reasons the Si-II to Si-III/Si-XII transformation during unloading will largely not be effected for microscale indents. However, the formation of the high pressure phases on unloading will certainly be inhibited at the very near surface and this surface H may be responsible for the difficulty in producing Si-III/Si-XII phases during unloading in nanoscale (<50 nm) indentations in ion-implanted relaxed a-Si.[15]

During indentation loading ion-implanted a-Si phase transforms to a metallic phase (Si-II). The volume of Si-II beneath the indenter tip then further transforms to Si-III/Si-XII (for conditions in this study) during unloading. Thus, if the transformation from a-Si to Si-II does not occur during loading, Si-III/Si-XII cannot be formed during subsequent unloading. Indeed, this has been found to be the case in unrelaxed ion-implanted a-Si where a plastic deformation via plastic flow rather than a phase transformation is favored during loading.[11] It is possible then that the increasing H content in relaxed a-Si inhibits the phase transformation to Si-II during the loading cycle and therefore reduces the formation of Si-III/Si-XII on unloading. However, changes in the plastic deformation mechanisms during loading are detectable in the load versus depth data. For example, unrelaxed ion-implanted a-Si that does not phase transform is significantly softer than relaxed a-Si. However, no evidence for a difference in the mechanical response during loading with increasing H concentration is observed in this study strongly suggesting that the a-Si will phase transform to Si-II and that the volume of Si-II formed during loading will be approximately the same in all samples. Therefore, the decrease in probability of forming detectable volumes of Si-III/Si-XII and the decrease in volume fraction of these phases with increasing H concentration suggests that the nucleation and/or growth of the phases is inhibited by the presence of H (see more below) and that a higher volume fraction of the Si-II transforms to a-Si during unloading.

This reduction in the fraction of Si-III/Si-XII in the phase transformed zone with increasing H content is observed in the Raman data, XTEM, and from changes in features on the unload curves. A clear pop-out on unloading is generally associated with the sudden formation of a substantial volume of Si-III/Si-XII. The lower density of these phases compared to Si-II results in a sudden volume expansion beneath the indenter tip. In this study these clear pop-outs evolve to kinklike features with increasing H concentration. At a H concentration of 5×10^{20} cm^{-3} the unload curves are featureless. Thus, as the volume of Si-III/Si-XII that is formed during unloading decreases, the magnitude of the pop-out/kink will correspondingly decrease. The evolution of these features on the unload curves with increasing H concentration correlate with the Raman and XTEM observations. In our recent study of the effect of O on the

indentation-induced phase transformations,[12] it was observed that the pop-outs were reduced in magnitude and were barely discernable with increasing O content. This was attributed to the formation of reduced volumes of Si-III/Si-XII formed within the transformed zone and correspondingly more a-Si. The XTEM images from selected indents in the current H study support these conclusions, notably the data from the indents taken from the 5×10^{19} and 5×10^{20} cm^{-3} H samples, where the volume fraction of Si-III/Si-XII in these indents is significantly lower than that of the H-free sample. As discussed above in relation to the loading curve, the phase transformed zones are comparable in size with those from H-free material but are composed of smaller volumes of Si-III/XII distributed within a mostly a-Si transformed zone. Interestingly, for the higher H concentration samples, the volumes of Si-III/XII are randomly distributed within the phase transformed zone. This is in contrast with the behavior in O-implanted samples, where the volumes of Si-III/Si-XII appeared to be located toward the periphery of the transformed zone.[12]

There are two possibilities that could explain this observation. First, the nucleation of the Si-III/Si-XII phases is inhibited such that the concentration of randomly located nucleation sites is reduced with increasing H concentration thereby reducing the total final volume of Si-III/Si-XII. Second, nucleation is unaffected but the subsequent growth rate of Si-III/XII during unloading is reduced with increasing H concentration. We suggest that the latter is the more likely scenario and that the inhibited growth of the Si-III/Si-XII grains is similar to that of solid phase crystallization of a-Si in the presence of H.[16] Almost all of the H is expected to be bonded to Si in a monohydride configuration (for [H] <3 at. %).[17] It has been shown previously that these Si-H bonds retard solid phase epitaxial crystallization of a-Si to diamond cubic Si-I with increasing H concentration above $\sim1\times10^{18}$ cm^{-3}.[16] A similar mechanism could be responsible for the retarded growth of Si-III/Si-XII from Si-II during indentation. Additionally, the solubility limit of H in c-Si is orders of magnitude lower than that in a-Si. Thus, during solid phase crystallization of a-Si, H segregates out of the crystalline Si-I phase and is pushed out ahead of the crystallization front decreasing the crystallization further. The solubility of H in Si-III/Si-XII (crystalline phases) is also likely to be low (these phases are more dense than crystalline Si-I) and a similar change in growth rate would be observed as H segregates out of the Si-III/Si-XII phases. It would be of interest to measure the H content in the Si-III/Si-XII phases following indentation and compare this to the solubility of H in crystalline Si-I.

Finally, the peak positions corresponding to the high pressure phases in the Raman spectra shift to lower wavenumbers with increasing H concentration above 5×10^{18} cm^{-3} (see Fig. 5) The peaks are approximately 1.5 cm^{-1} higher in the H-free indents than those from the indents made in the highest H concentration sample. Based on results from a study in which the peak position corresponding to Si-I was measured as a function of stress, the results here suggest that the Si-III/XII zones in the H-free case are in a higher compressive residual stress state (approx. 0.5 GPa).[18] The peak position for Si-XII in the H-free sample is at ~354 cm^{-1}, which is in close agreement with other Raman studies of nanoindentation-induced Si-XII phases.[19] As the H concentration increases, this peak position reduces to ~352.5 cm^{-1}, comparable to that of *stress-free* Si-XII formed in diamond anvil cells.[20,21] The volume expansion from formation of small volumes of Si-III/Si-XII (less dense than Si-II) from Si-II can be accommodated by plastic flow of the larger volume fraction of indentation-induced a-Si surrounding the Si-III/Si-XII. For larger volume fractions of Si-III/Si-XII, where less of the phases are surrounded by softer indentation-induced a-Si, the starting matrix accommodates the stress to a lesser degree. Hence, larger volumes of Si-III/Si-XII will be under greater compressive stress.

V. CONCLUSION

Amorphous Si films formed by ion-implantation and relaxed by thermal annealing, which are known to phase transform under the indentation conditions used in this study, have been further ion-implanted with H to increase the H concentration up to levels as high as 5×10^{20} cm^{-3} within the phase transformed zone. A reduction in volume fraction of Si-III/XII within the phase transformed zone is observed by Raman and XTEM with increasing H concentration. At a concentration of 5×10^{20} cm^{-3}, volumes of Si-III/XII are formed in only $\sim50\%$ of indents. The reduction in formation of the high pressure phases is accompanied by a decrease in occurrence of large pop-out events on the unloading curve and a trend to smaller kinklike events. These smaller events are the result of the reduced volume of Si-III/XII forming in the residual indents. Finally, XTEM images from selected indents reveal that the reduced volume of Si-III/XII in the phase transformed zones is randomly distributed within the phase transformed zone with the remaining volume composed of a-Si. We suggest that the growth of Si-III/Si-XII crystallites from nucleation sites is retarded by the presence of increasing H concentration by a mechanism similar to that in retarded solid phase crystallization of a-Si.

ACKNOWLEDGMENTS

The authors are grateful to funding from the Australian Research Council. We also thank P. Munroe for the use of TEM sample preparation facilities at UNSW and B. Haberl for XTEM sample foil preparation.

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