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Effect of oxygen concentration on nanoindentation-induced phase transformations in ion-implanted amorphous silicon

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The effect of the local oxygen concentration in ion-implanted amorphous Si (*a*-Si) on nanoindentation-induced phase transformations has been investigated. Implantation of oxygen into the *a*-Si films has been used to controllably introduce an approximately constant concentration of oxygen, ranging from $\sim 10^{18}$ to $\sim 10^{21}$ cm^{-3}, over the depth range of the phase transformed zones. Nanoindentation was performed under conditions that ensure a phase transformed zone composed completely of Si-III/XII in the nominally oxygen-free *a*-Si. The effect of the local oxygen concentration has been investigated by analysis of the unloading curves, Raman microspectroscopy, and cross-sectional transmission electron microscopy (XTEM). The formation of Si-III/XII is suppressed with increasing oxygen concentration, favoring a greater volume of *a*-Si within the zones. The Raman microspectroscopy and XTEM verify that the volume of Si-III/XII decreases with increasing O concentration. With the smaller volumes of Si-III/XII, the pop-out normally observed on load versus penetration depth curves during unloading decreases in magnitude, becoming more kinklike and is barely discernable at high concentrations of oxygen. The probability of forming any high pressure phases is reduced from 1 to ~0.1 for a concentration of 10^{21} cm^{-3}. We suggest that the bonding of O with Si reduces the formation of Si-III/XII during unloading through a similar mechanism to that of oxygen-retarded solid phase crystallization of *a*-Si. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3097752]

I. INTRODUCTION

There has been significant interest over recent years in nanoindentation-induced phase transformations in Si with more recent studies on nanoindentation of ion-implanted amorphous Si (*a*-Si).[1–13] 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 *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.[2,3,5] These pressure-induced transformations are of great interest and workers have investigated the transformation pathways,[1,4,6–13] but the exact mechanisms behind the phenomena are still not well understood.

More recently, studies that have compared the nanoindentation-induced phase transformations in crystalline Si (*c*-Si) and ion-implanted *a*-Si have revealed that both materials undergo similar phase transformations during loading and subsequent unloading. On unloading, however, the high pressure crystalline phases (Si-III/XII) form much more readily during indentation in an *a*-Si matrix, e.g., 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.[10,11]

Recent work by the current authors on plasma enhanced chemical vapor deposited (PECVD) *a*-Si films found that the films do not undergo these phase transformations. The reasons for this are not understood but one possibility is that the high impurity content in the deposited films compared to a "pure" film created by ion implantation prevents the formation of the high pressure phases. In particular, O and H are found in high concentrations (10^{19}–10^{21} cm^{-3}) in PECVD films compared to $\leq 10^{18}$ cm^{-3} in *a*-Si formed by Si ion implantation. The aim of this study is to quantitatively study the effect of O while separating this from the effects caused by other impurity content and variations in *a*-Si microstructure. This is done through ion implantation of O into ion-implanted *a*-Si, controllably adding a range of O 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 O-free 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 O 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 layer of *a*-Si was created by multiple energy implantation of Si. Samples were then cleaved and implanted with O. Implantation of O was performed at 15, 30, 50, and 100 keV to fluences, which created an approximately constant concentration of O from 30 to 350 nm below the surface ($\sim 10^{18}$, 10^{19}, 10^{20}, and 10^{21} cm^{-3}). These concentrations cover those

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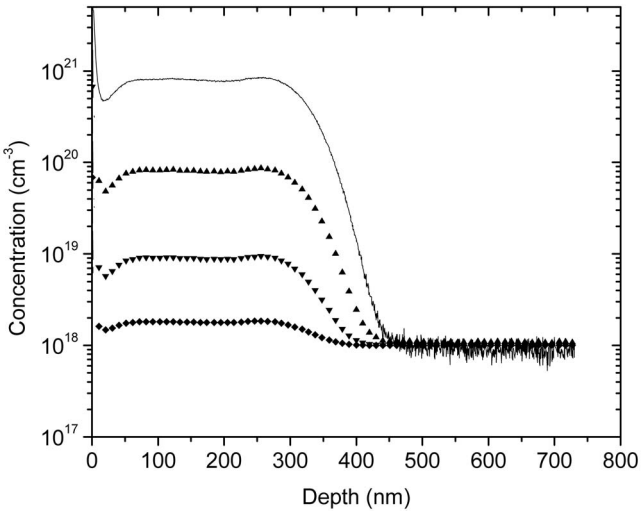

FIG. 1. Oxygen concentration-depth profiles of the implanted samples measured by secondary ion mass spectrometry. The depth profile for each of the oxygen implanted samples is shown. Each sample is referred to in this paper by the approximate maximum in the O concentration profile, i.e., 10^{21}, 10^{20}, 10^{19}, and 10^{18} cm^{-3}. The background O concentration in the 2 μm *a*-Si layer is $\sim 10^{18}$ cm^{-3}.

typically found in deposited *a*-Si samples made by various *a*-Si deposition methods. The concentration-depth profiles for all oxygen implanted samples following a relaxation annealing of 450 °C for 30 min are shown in Fig. 1 (this annealing transforms the as-implanted *a*-Si to a relaxed state which is required for phase transformations during indentation). The concentration-depth profiles are extremely reproducible because of the high control of ion-implant energy and dose. The background level of O in the ion-implanted layer is $\sim 1 \times 10^{18}$ cm^{-3} which is in agreement with the typical levels reported for Czochralski grown Si wafers [ranging from 5×10^{17} to 10^{18} cm^{-3} (Ref. 14)]. The final set of samples consisted of a sample containing no additionally implanted O (labeled *a*-Si) and O implanted samples which are referred to by the approximate concentration of O over the most uniform region of the implanted layer.

Indentation was performed using an Ultra-Micro-Indentation-System (UMIS) 2000 fitted with an $\sim$4.3 μm radius spherical tip. Loading in 10 increments to 80 mN (an average loading rate of 3.6 mN/s) was followed by unloading in 40 increments (an average unloading rate of 0.9 mN/s). These conditions typically result (for *a*-Si containing a low oxygen content) 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.[10,11,15] A prime indicator for the formation of these phases during unloading is the presence of a pop-out on the unloading curve. The formation of Si-III/XII proceeds through a nucleation and growth process which results in a variation in final microstructure between indents made under identical conditions. Therefore, the probability of a pop-out occurring during unloading and the formation of Si-III/XII was extracted from both 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 $\sim$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.[16,17] The samples were then imaged using a Philips CM 300 transmission electron microscope.

III. RESULTS

It is appropriate to comment on the pop-outs that are observed in these indentation experiments. Figure 2(a) shows the examples of load/unload curves measured during these experiments and shows the differences in the form of the "pop-out" events. For indentation in the samples used in this study, the pop-outs exhibit variations in position, size, and shape. During unloading many pop-outs were less pronounced and appeared as a kink in the unloading cycle and in some cases were difficult to differentiate from an unload curve with no pop-out unless the derivative of the unload curve was taken. Examples of these small kinks are illustrated in Fig. 2(b) which shows examples of the derivative of the unload curves for those containing kinks as well as those that have no features on the unloading curve. The occurrence of kinks in the unload curves increases for the samples containing increased concentrations of O. We will return to this point later in Sec. IV. Apart from differences in the form of the pop-out event on unloading, the overall mechanical response of the samples (all O concentrations) did not change, i.e., the load/unload curves were the same shape with the same maximum penetration depth. This suggests that the *a*-Si transforms to a metallic phase (Si-II or a high density *a*-Si phase) on loading, as we will discuss later.

Figure 3 shows the probability of a clear pop-out/kink (i.e., those that are observable by eye without having to examine the derivative of the unloading curve) occurring on unloading with the probability of detecting Si-III/Si-XII by Raman as a function of implanted O concentration. The probability of a pop-out occurring decreases monotonically with increasing O concentration and reaches 0 for a concentration of 1×10^{21} cm^{-3}. However, the probability of detecting Si-III/XII in the residual indents remains at $\sim$1 except for the 1×10^{21} cm^{-3} sample for which this probability is $\sim$0.1. Also shown is the probability of the occurrence of either a pop-out or a "kink," where the latter is only detected by examining the derivative of the unload curve [e.g., Figure 2(b)]. This probability follows that of detecting Si-III/XII by Raman except for the 10^{21} cm^{-3} sample.

An indication of the volume fraction of Si-III/XII in the phase transformed zones can be estimated from the intensity of the Raman peaks associated with the high pressure phases. Figure 4 shows the average intensity of the Raman peak at 350 cm^{-1} (corresponding to Si-XII but with an intensity rep-

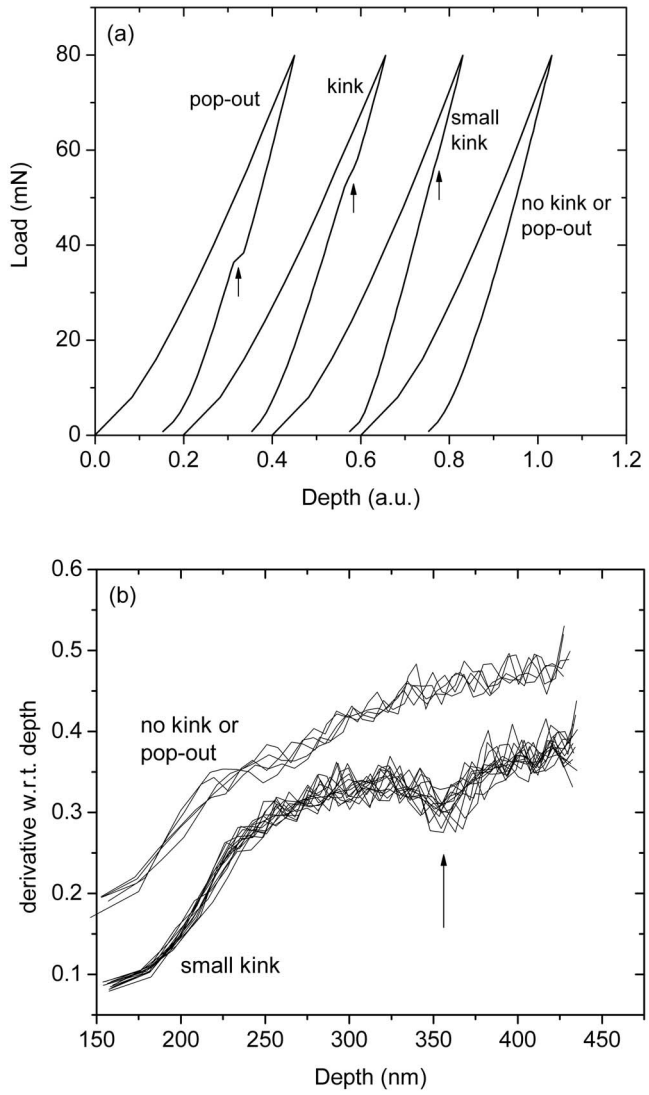

FIG. 2. (a) Representative load/unload curves for indents made in the *a*-Si samples (each curve is shifted along the depth axis for clarity). The overall curves are the same except for the pop-out events during unloading. Examples of clear pop-outs, kinks, and no kink/pop-outs are shown (those features are marked by an arrow on the unloading curve). The pop-outs and larger kinks are clearly observable by the eye on the unloading curves. However, the small kinks are not discernable and the unloading curves look the same as those with no kinks or pop-outs. (b) shows examples of derivatives of the unload curves for those indents containing small kinks and no kinks or pop-outs. The change in slope of the unloading curve can be seen in the derivative for the small kinks (marked by arrow).

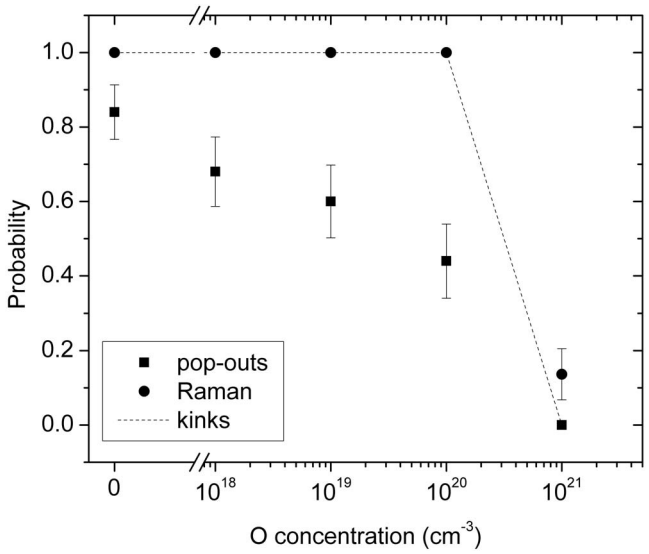

FIG. 3. Probability of observing clear pop-outs (observable by eye on the unloading curve), kinks (observed either on the unload curve or by examining the derivative of the unload curve) during unloading, and Si-III/XII in the residual indents measured by Raman as a function of average O concentration in the phase transformed zone (extracted from measurements of 25 indents). The number of clear pop-outs decreases with O concentration. No significant changes in occurrence of pop-outs plus kinks and detection of Si-III/Si-XII are observed for O concentrations $<10^{20}$ cm^{-3}. For the sample containing 10^{21} cm^{-3} O, no features on the unload curves are observed and only ~10% of the indents contained Si-III/XII.

resentative of all peaks associated with Si-III and Si-XII in this study) as a function of O concentration in the *a*-Si film for those indents in which high pressure phases were detected. The intensity and therefore the approximate volume of Si-XII (and Si-III from peaks associated with this phase—data not shown here) decrease with O concentration and for the 1×10^{21} cm^{-3} sample the intensity is about 5% of that of the O-free sample. For this concentration the probability of forming high pressure phases is also reduced from 1 to ~0.1. In addition, the variation in intensity over the 25 indents per sample (error bars) decreases with increasing oxygen content.

Figure 5 shows the position of the most intense Si-XII Raman peak as a function of O concentration. The average peak position decreases in wavenumber as the O concentration increases and decreases by ~2 cm^{-1} for the highest O concentration samples (1×10^{20} and 1×10^{21} cm^{-3}). The position of the peaks corresponding to the high pressure phases in the Raman spectra is related to the residual stress levels in the phase transformed zones.[18]

Figure 6 shows the bright-field XTEM images of selected indents made in O-free *a*-Si and *a*-Si implanted with

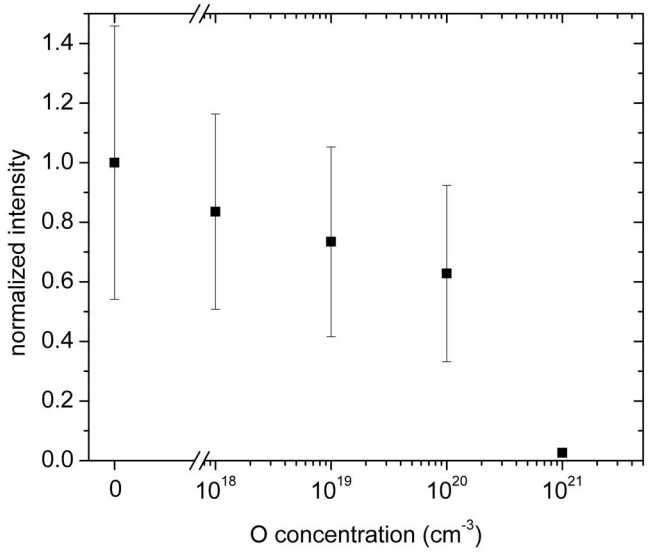

FIG. 4. Average intensity of the peak corresponding to Si-XII (at 350 cm^{-1}) in the Raman spectra as a function of O concentration in the *a*-Si (normalized to the peak intensity from the O-free sample). These data are extracted from the 25 spectra taken for each sample. The peak intensity (representative of the volume of both high pressure phases) decreases with increasing O content.

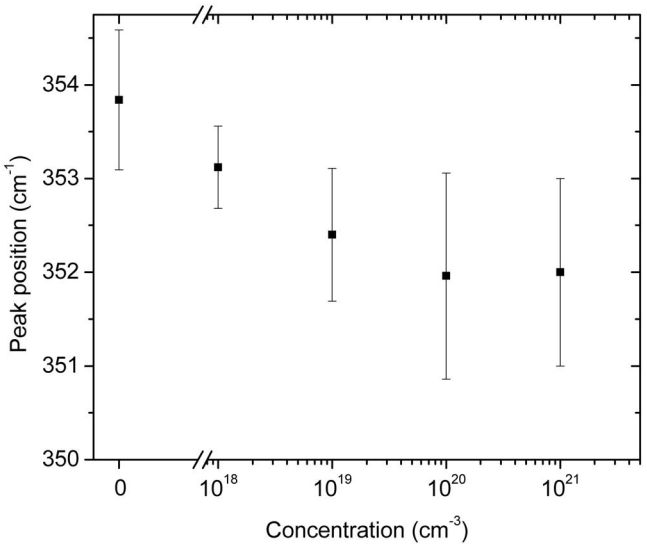

FIG. 5. Peak position of the large Si-XII peak (at 350 cm^{-1}) as a function of O concentration. The position of this peak is related to the residual stress state of the high pressure phases in the end zone. The peak position shifts to lower wavenumbers with increasing O concentration up to a level of 10^{20} cm^{-3}.

O to concentrations of 10^{20} and 10^{21} cm^{-3}. For the 25 indents made in the 10^{21} cm^{-3} samples, only three contained Si-III/XII. For the O-free samples, a substantial volume (roughly the whole transformed zone) of the phase transformed zone contains Si-III/XII in agreement with previous studies.[10,11,15] For the indent from the 10^{20} cm^{-3} sample, a substantial fraction of the phase transformed zone is composed of *a*-Si and for the 10^{21} cm^{-3} only a thin layer at the lower periphery of the zone is composed of Si-III/XII. Although these XTEM images are from selected indents from 25 samples, they do illustrate the reduced volume of Si-III/XII formed in the phase transformed zones containing high concentrations of O, in agreement with the Raman data.

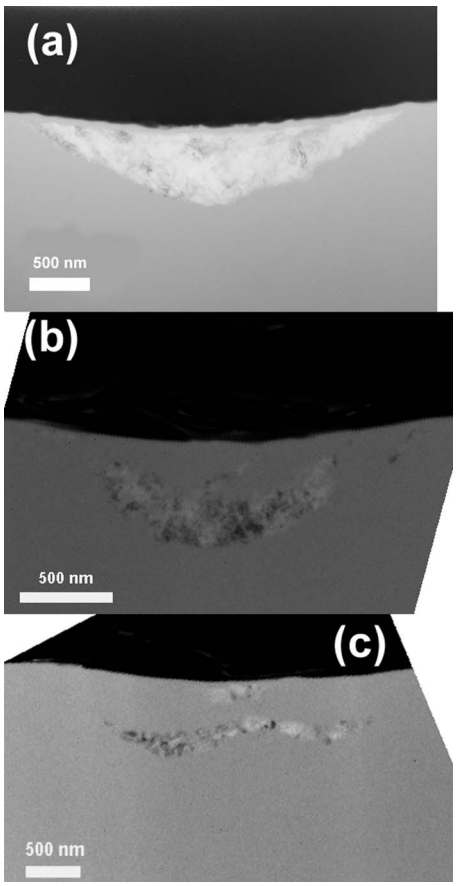

FIG. 6. Bright-field XTEM images for selected indents. (a) The final phase transformed zone of an indent made in the O-free a-Si sample, i.e., the background level of O is $\sim 10^{18}$ cm^{-3}. This final structure is typical for these indentation conditions and has been observed in many other studies by the authors (Refs. 10 and 15). (b) The phase transformed zone of one of the indents containing Si-III/XII (measured by Raman) made in the 10^{20} cm^{-3} sample. The volume fraction of Si-III/XII is reduced compared to that of the indent in (a). (c) A similar XTEM image for the 10^{21} cm^{-3} sample. Here, a greatly reduced volume of Si-III/XII is formed and is located at a depth >350 nm where the local O concentration is dropping off toward the background level.

IV. DISCUSSION

Increasing the O content above the levels typically found in Czochralski grown Si wafers affects the formation of Si-III/XII during nanoindentation unloading. With increasing concentration, the volume fraction of Si-III/XII in the phase transformed zone decreases, the residual stress in the final material is reduced, and at high concentrations ($>10^{20}$ cm^{-3}) formation of the phases appears to be completely inhibited.

The decrease in intensity of the Raman peaks associated with the Si-III/XII phases with increasing O concentration correlates with the decrease in occurrences of clear pop-outs during unloading. The pop-out is believed to be the result of the sudden formation of a substantial volume of Si-III/XII (>95% of the entire zone) in the phase transformed zone. The high pressure phases have a lower density than the metallic phase formed during loading, causing a volume increase and therefore pop out when they are formed. If the volume of Si-III/XII formed during unloading is reduced, it is expected that the magnitude of the pop-out decreases. This is observed here with the clear pop-outs evolving to smaller kinks on the unloading curve with increasing O content. In addition, pop-outs were never detected for the indents made in the highest O concentration (10^{21} cm^{-3}) sample. This suggests that smaller volumes of Si-III/XII are formed with increasing O content and for the highest concentration the formation of the phases is substantially inhibited. The Raman measurements on all of the indents and XTEM images taken from selected indents support this, both techniques showing reduced volumes of Si-III/XII in the residual indents with increasing O concentration. The starting *a*-Si (which has a background level of O of $\sim 10^{18}$ cm^{-2}) forms a substantial volume of Si-III/XII for all indents made under the indentation conditions used here. The effect of increasing O from this background concentration in this study suggests that the probability of formation of the high pressure phases may be enhanced further (e.g., the phases may be formed more readily for rapid unloading) by reducing the O concentration to levels below 10^{18} cm^{-2}. This could be tested by nanoindentation of *a*-Si layers formed in float-zone grown wafers where the O levels are several orders of magnitude lower than those in Czochralski grown wafers.

When the *a*-Si transforms to a metallic phase during loading, it is unclear whether this phase is Si-II or a high density *a*-Si phase.[4,19,20] However, this metallic phase does transform to Si-III/XII during unloading.[10,11,15,19] We note that the Si-III and Si-XII phases only form from such a metallic phase during unloading. Therefore, it could be possible when no Si-III/Si-XII is observed at high O concentrations, that the reduced high pressure phase formation is due to O inhibiting the transformation from *a*-Si to the metallic phase during loading. However, this seems unlikely as no change in mechanical response of the Si is observed in the load/unload data, whereas it was shown previously that when unrelaxed ion-implanted *a*-Si does not transform during loading, the material is significantly softer.[15] The likely scenario then is that the metallic phase does form during loading (and is largely unaffected by oxygen) whereas the formation of Si-III/XII is effected by the O during unloading. This also means that when no Si-III/Si-XII is detected by Raman in the residual indents, the indented zone is composed only of *a*-Si which has formed from the metallic phase during unloading. Additionally, when reduced volumes of Si-III/XII are measured, the remainder of the transformed zone, which is composed of *a*-Si, is also formed through phase transformation from a metallic Si phase.

Following implantation, the O atoms are likely to bond with the host Si atoms when there are a large number of dangling bonds from implantation disorder.[21] The presence of high concentrations of O ($\sim$0.5 at. %) in *a*-Si has been found previously to retard thermally induced solid phase crystallization by an order of magnitude.[22] Strong Si–O bonds in this crystallization case affect the kinetics of bond breaking required for rearrangement of atoms in the *a*-Si to the crystalline form.[22,23] A similar mechanism, caused by strong Si–O bonds, can be envisaged here to inhibit the bond rearrangement required for the transformation of the metallic phase to the high pressure crystalline phases, Si-III and Si-XII, noting that the highest concentration of O in this study (10^{21} cm^{-3}) corresponds to 2 at. %.

The peak positions corresponding to the high pressure phases in the Raman spectra (Fig. 5 shows the peak position of the large Si-XII peak) shift to lower wavenumbers with increasing O concentration. The peaks are approximately 2 cm^{-1} higher in the O-free indents than those from the indents made in the highest O concentration samples. Based on the results from a study in which the peak position corresponding to Si–I was measured as a function of stress, the results here indicate that the Si-III/XII zones in the O-free case are in a higher compressive residual stress state (approximately 0.5 GPa).[18] The peak position for Si-XII in the O-free sample is at $\sim$354 cm^{-1}, which is in close agreement with other Raman studies of nanoindentation-induced Si-XII phases.[24,25] As the O concentration increases, this peak position reduces to $\sim$352 cm^{-1}, comparable to that of *stress-free* Si-XII formed in diamond anvil cells.[26,27] The lower density of Si-III/Si-XII, compared to *a*-Si and the metallic phase, results in a phase transformed zone which is under compressive stress if a substantial volume fraction of the zone is composed of higher density Si-III/XII phases. Therefore, it would be expected that as this volume fraction is reduced, the Si-III/XII will be under correspondingly less residual stress.

A final observation is related to the location of the volumes of Si-III/XII formed in the higher O concentration samples (10^{20} and 10^{21} cm^{-3}). The phase transformed zone is composed of *a*-Si and a fraction of Si-III/XII, which is located at depths at or near the periphery of the phase transformed zone (Fig. 6). The concentration of O decreases over the depth range of 350–500 nm where it then reaches a bulk concentration of 10^{18} cm^{-3} (Fig. 1). This depth region coincides with the location of the volumes of Si-III/XII that are formed in the phase transformed zones of higher concentration samples (Fig. 6). The lower concentrations of O in this zone provides conditions that would favor the formation of Si-III/XII as observed for the whole transformed zone in the lower O concentration samples. Although there are limited TEM data, Figs. 6(b) and 6(c) indicate that the formation of Si-III/XII is retarded when the local O concentration is greater than $\sim 8 \times 10^{19}$ cm^{-3} (using the concentration-depth profiles from Fig. 1). Therefore, by extending the depth of the O concentration profile, the formation of Si-III/XII in the entire phase transformed zone may be prohibited for the particular indentation conditions used here. This also provides an opportunity to selectively form Si-III/XII within subregions of the entire phase transformed zone by tailoring the O implant profiles.

V. CONCLUSION

a-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 O to increase the O concentration up to levels as high as 10^{21} 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 microspectroscopy and XTEM with increasing O concentration. At a concentration of 10^{21} cm^{-3}, volumes of Si-III/XII are formed in only $\sim$10% of the indents compared to 100% in the O-free *a*-Si. 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 kink-like events. These smaller events are the result of the reduced volume of Si-III/XII forming in the end zone. Finally, XTEM images from selected indents reveal that the Si-III/XII material that does form in the zones in the higher O concentration samples is located at depths where the O concentration begins decreasing with depth.

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