Effect of oxygen on nanoscale indentation-induced phase transformations in amorphous silicon

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ABSTRACT

Ion-implantation has been used to introduce oxygen concentration-depth profiles into nominally oxygen-free amorphous silicon (a-Si). The effect of O concentrations in excess of \(10^{18}\) cm\(^{-3}\) on the formation of high pressure crystalline phases (Si-III and Si-XII) during indentation unloading has been studied. By examination of unloading curves and post-indent Raman microspectroscopy O is found to inhibit the so-called pop-out event during unloading and, therefore, the formation of the crystalline phases. Furthermore, at high O concentrations (> \(10^{21}\) cm\(^{-3}\)) the formation of these phases is reduced significantly such that under indentation conditions used here the probability of forming the phases is reduced to almost zero. 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.

INTRODUCTION

Nanoindentation-induced phase transformations in Si have attracted significant interest over the last few decades with more recent studies reported in nanoindentation of ion-implanted amorphous Si (a-Si) [2-6]. During loading, a transformation to the \(\beta\)-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 favoured for slow unloading and is usually accompanied by a pop-out event [2, 3]. These pressure-induced transformations are well characterized [2-6], but the exact mechanisms behind the phenomena are still not well understood. In particular the proposed formation of the crystalline phases by a nucleation and growth mechanism has not been studied in detail.

Recent studies have investigated these phase transformations during indentation of ion-implanted a-Si [5, 7]. It was found that the Si-III/Si-XII phases form more readily in an a-Si matrix compared to c-Si e.g. volumes of Si-III/Si-XII formed in a-Si with unloading rates over 3 orders of magnitude greater than the unload rates required to form the phases in c-Si. However, recent work by the current authors on plasma enhanced chemical vapour 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 (\(10^{19}\) to \(10^{21}\) cm\(^{-3}\)) in PECVD deposited films compared to \(<10^{18}\) cm\(^{-3}\) in a-Si formed by Si ion-implantation [8]. The aim of this study is to study the effect of O on the indentation-induced phase transformations. This is done through ion-implantation of O in to 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 a high probability of forming Si-III/XII in the phase transformed zones for nominally O-free ion-
implanted a-Si. Analysis of the load/unload curves and Raman micro-spectroscopy are used to study the effect of O on the phase transformation behaviour.

EXPERIMENT

All samples were fabricated in a 7 μm epi-layer p-doped with boron to a resistivity of 10-20 Ω-cm grown on a low resistivity (0.002 Ω-cm) Si(100) wafer. A 350 nm 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 30 and 50 keV to total fluences of 3.1x10^14, 3.1x10^15, and 3.1x10^16 cm^-2 corresponding to peak O concentrations of ~2x10^19, 2x10^20, and 2x10^21 cm^-3 (fig. 1). These concentrations cover those 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 anneal of 450 °C for 30 minutes [9] are shown in figure 1. 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 total implanted fluence.

Indention was performed using a Hysitron Triboindenter fitted with a Berkovich diamond tip. Loading to 4 mN (and 7 mN) and unloading at 0.2 mN/s was repeated 54 times in each sample. These conditions form a phase transformed zone that extends 150 nm below the surface and has a diameter of ~400 nm for the 4 mN maximum load (the zone extends approximately 250 nm below the surface for 7 mN). These zones have been imaged using XTEM (not shown here). Typical load/unload curves and indentation hardness data are shown in figure 2 for the samples. These loading conditions result in a probability of pop-out during unloading of ~0.4 for nominally O-free a-Si of thickness 350 nm (approx. 0.8 for 7mN). 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 the series of 54 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
\( \mu m \) diameter (power 2.1mW). These measurements provide a method for detecting the presence of Si-III/XII. The measurements can also be correlated with the load/unload curves from the indentation tests.

![Figure 2](left) Typical load/unload curves for indentation in all samples. A pop-out is observable for this example for the 7mN indent. (right) Indentation hardness versus depth data for all samples extracted from a series of indents with increasing load up to \(-10 \) mN. No appreciable difference in mechanical properties is observed across samples.

RESULTS AND DISCUSSION

Figure 3 shows the probability of a pop-out occurring as a function of implanted O fluence for loading to 4 mN and unloading at a rate of 0.2 mN/s. The probability of a pop-out occurring decreases with increasing O content. For a fluence of \( 3.1 \times 10^{15} \) cm\(^{-2} \) (corresponding to a peak O concentration of \( \sim 2 \times 10^{21} \) cm\(^{-3} \)) the probability is reduced to only \( \sim 0.03 \) which is comparable to that of c-Si (also shown in fig. 3).

![Figure 3](Probability of observing a pop-out event during unloading as a function of total implanted O fluence. Unloading from 4 mN at a rate of 0.2 mN/s was performed and the data were extracted from 54 indents made in each sample. Also, shown is the probability of a pop-out for indentation in c-Si.)

Figure 4 shows typical Raman spectra taken from indents made in nominally O-free and O-implanted a-Si samples at two different maximum loads (4 and 7 mN). For the O-free a-Si,
extra peaks associated with Si-III/Si-XII are visible around 350-420 cm⁻¹. The peaks are more intense for the larger indents due to the larger volumes of Si-III/Si-XII formed in these indents. For a maximum load of 4 mN, these peaks are not visible in the spectra taken from all fluences of O-implanted samples. This means that any Si-III/Si-XII in the residual indents is formed at volumes below the detection limit for Raman. For the larger indents, Si-III/Si-XII is visible in the spectra for the 3.1x10¹⁴ and 3.1x10¹⁵ cm⁻² samples. However, the volume clearly decreases with increasing O until no Si-III/Si-XII is detected for the 3.1x10¹⁶ cm⁻² sample.

Figure 4. Typical Raman spectra taken in unindented a-Si and indents in samples with increasing O concentration. The left panel is for data taken in 4 mN indents. The right panel shows data for 7 mN indents. The small peaks between 300 and 400 cm⁻¹ are associated with Si-III and Si-XII.

Figure 5 summarizes the Raman data taken on the indents made at 4 and 7 mN. The probability of detecting Si-III/XII in the indents decreases from 1 to 0 at a O fluence of 3.1x10¹⁴ cm⁻² for loading to 4 mN. For the larger indents made at 7 mN, this decrease occurs between 3.1x10¹⁵ and 3.1x10¹⁶ cm⁻².

Although not all of the O-free indents exhibit a clear pop-out event (fig. 2 and 3), Si-III/Si-XII was detected in all indents made in the O-free sample (see fig. 5). It has been shown previously that Si-III/XII can still be formed in the absence of a clear pop-out e.g. for indentation at elevated temperatures or when only a small fraction of the phase transformed zone transforms to Si-III/XII [10, 11]. It was suggested that in these cases, the Si-III/Si-XII was formed in a more continuous fashion than a sudden catastrophic formation of a substantial volume. In addition, the current authors have never observed the absence of Si-III/Si-XII (from Raman and transmission electron microscopy measurements) when a pop-out occurs on unloading. Although Si-III/Si-XII is not detected by Raman in many of these implanted samples, it is likely that Si-III/Si-XII is still formed in the indents that exhibit a pop-out on unloading but at a volume below the Raman detection limit.

For many load/unload curves (not shown here) the pop-out is more kink-like as the O content increases. The pop-out event is associated with the sudden formation of a substantial volume of Si-III/Si-XII. The density of these phases is lower than that of the Si-II which forms under the indenter tip during loading. Thus, the transformation of a significant volume of Si-II to Si-III/XII results in a volume increase beneath tip and forces it out from the surface. The
magnitude of the pop-out event will thus decrease as the volume of Si-III/Si-XII formed decreases.

The larger volume and more ready detection of Si-III/XII in the 7 mN indents is likely a result of two factors. One, the volume of Si-II formed during loading is larger which promotes the formation of Si-III/XII; two, the phase transformed zone extends to a depth where the O concentrations decrease to the background level. In this region the formation of Si-III/XII is inhibited to a lesser degree than at the peak of the O concentration profile (at a depth of ~100 nm).

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 [12, 13]. However, this metallic phase does transform to Si-III/XII during unloading [5, 7, 12, 14]. 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 doesn’t transform during loading, the material is significantly softer [14]. The measured hardness versus contact depth for a series of indents made in nominally O-free a-Si and O implanted samples is shown in fig 2. These data indicate then 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. 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.

The presence of high concentrations of O (~0.5 at. %) in a-Si has been found previously to retard thermally induced solid phase crystallization by an order of magnitude [15]. Strong Si-O bonds, such as those that will be formed here, affect the kinetics of bond-breaking required for rearrangement of atoms in the a-Si to the crystalline form [15, 16]. A similar mechanism 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. %.
CONCLUSIONS
The effect of local O concentration on the nanoindentation-induced phase transformations in ion-implanted a-Si has been studied. Ion-implantation of O has been used to create concentration-depth profiles extending to ~200 nm below the surface with peak concentrations of up to $2 \times 10^{21} \text{ cm}^{-2}$. The probability of the occurrence of a pop-out, indicating the formation of Si-III/Si-XII during unloading, decreases with increasing O content. Raman measurements made on residual indents confirm that the volume of Si-III/Si-XII formed decreases with oxygen content. 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.

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9. This anneal converts the a-Si to a relaxed state which is required for subsequent phase transformation during indentation.
Measuring Local Mechanical Properties Using FIB Machined Microcantilevers

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ABSTRACT

Micro-scale Focused Ion Beam (FIB) machined cantilevers were manufactured in single crystal copper, polycrystalline copper and a copper-bismuth alloy. These were imaged and tested in bending using a nanoindenter. Cantilevers machined inside a single grain of polycrystalline copper were tested to determine their (anisotropic) Young’s modulus: results were in good agreement with values calculated from literature values for single crystal elastic constants. The size dependence of yield behavior in the Cu microcantilevers was also investigated. As the thickness of the specimen was reduced from 23μm to 1.7μm the yield stress increased from 300MPa to 900MPa. Microcantilevers in Cu-0.02wt%Bi were manufactured containing a single grain boundary of known character, with a FIB-machined sharp notch on the grain boundary. The cantilevers were loaded to fracture allowing the fracture toughness of grain boundaries of different misorientations to be determined.

INTRODUCTION

Much recent work on measuring mechanical properties on the microscale has been carried out using focused ion beam (FIB) machining to manufacture a wide range of different tests specimens[1-3] which are then tested using a nanoindenter as a loading device. This is of great interest as it allows mechanical properties to be measured from much smaller volumes than are required for traditional mechanical tests. It is now possible to measure directly the mechanical properties of individual microstructural features such as grains, grain boundaries or thin layers, such as ion-implanted layers in bulk specimens [4].

A recent paper [5] by the present authors has demonstrated that testing of microcantilevers with a triangular cross section, machined into the surface of single crystal copper, can be used to measure the anisotropy of Young’s modulus with respect to crystallography. This paper describes the extension of such techniques to measure plastic and fracture properties as well as Young’s modulus.

EXPERIMENT

Materials

Three materials were chosen as model systems for developing microcantilever-testing techniques. For measuring elastic properties high purity polycrystalline copper was chosen. This was easily prepared and is well known for having highly anisotropic elastic properties. Single crystal copper was used for carrying out measurements into size effects in plastic properties. This allowed all cantilevers to be made with the same crystallography to avoid the influence of crystal anisotropy. For measuring grain-boundary fracture properties Cu-Bi was chosen, as it is well
known that a small amount of bismuth (less than 0.1 wt%) [6] causes grain boundary embrittlement at room temperature.

**Bulk Sample Preparation**

The single crystal copper (99.9999%) was prepared by first mechanically polishing with diamond pastes of decreasing size from 8|Lim to 1|um. This was followed by electropolishing using 1.2V and 0.1A for 30 seconds in a solution of 80% ortho-phosphoric acid, producing a smooth surface free from mechanical deformation. EBSD was used to confirm the surface normal as [110] and to indentify the in-plane [001] and [1 1 0] directions.

Polycrystalline copper bar (99.9999%) was annealed at 800°C for 1 hour in argon to produce a large-grain sample. It was then sectioned to 500um thick discs, which were ground on SiC paper of 1200 grit, followed by vibropolishing on colloidal silica for 24 hours. EBSD was used to determine the average grain size (~200um) and to confirm that the surface was free from mechanical deformation.

To manufacture the copper-bismuth alloy, 9.7g of Cu and 3.7mg of Bi were sealed together in an evacuated clean quartz tube. This was heated in an argon atmosphere at 1100°C for 1 hour and then slow-cooled to room temperature. This produced an ingot of 4mm diameter, which was swaged to reduce the diameter to 3mm, producing an elongated grain structure with most grain boundaries running along the length of the ingot. The ingot was sectioned using a slow saw and polished using SiC paper to 1200 grit and then colloidal silica on a vibropolishing wheel for 24 hours. This was used as electropolishing has been shown to alter boundary chemistry in copper-bismuth alloys [7]. The sample was kept in the cold worked state to ensure boundaries were very close to normal of the surface.

**FIB Machining Of Microcantilevers**

Each microcantilever was manufactured using a FIE FIB200. For the studies into elastic and plastic properties the same beam design was used: a cantilever of triangular cross section machined into the surface of a bulk sample. Large beam currents, typically 3000pA to 5000pA, were used for the initial steps. First a “U” shaped trench was milled. The sample was then tilted to 30° and undercut from each side. Smaller beam currents, 300pA to 1000pA, were then used to clean each side of the cantilever to remove any redeposited material. For measuring elastic properties of copper a standard cantilever size was used, with width 3μm, thickness 3.5μm and length 27μm. These were placed inside 4 different grains, which were identified using EBSD, Figure 1 d. This then allowed the crystallographic direction of the long angle of the cantilever to be found. Size effects in yield stress were measured using cantilevers of varying size ranging from 1μm wide, 1.7μm thick and 10μm long to 25μm wide, 22μm thick and 100μm long. These were made with the long axis in the [110] direction in the single crystal copper, Figure 1 c.

For the study into fracture properties the microcantilevers were machined so as to contain a single grain boundary approximately 1μm from the fixed end. Cantilevers had a pentagonal cross section as used in the fracture studies of Di Maio and Roberts [1] so that cracks would initially propagate with constant width. Cantilevers with a width of 4.5μm length, thickness of 5μm and length of 20μm were made with a Zeiss Nvision40. The undercutting was performed at an angle of 30°. A sharp notch was machined on the grain boundary in a single pass using a beam...
current of 10pA for 60 seconds; this can be seen in figure 1a. This notch was found to be 700-800nm deep. Each cantilever was imaged using an SEM before testing to allow the width and thickness to be measured. EBSD was used to measure the misorientation across the grain boundary, and the boundary plane.

Figure 1: a) 6 cantilevers of differing size for measuring size effect in yield stress, b) EBSD showing single crystal cantilevers cut from polycrystalline copper for measuring anisotropy in Young’s modulus, c) Microcantilever with pentagonal cross section and sharp notch at grain boundary for measuring fracture toughness, d) EBSD of cantilever for fracture toughness measurements showing position of grain boundary.

Testing Of Microcantilevers

All the microcantilevers were tested using a AFM/nanoindenter (MTS nano XP). Cantilevers were first located using the optical microscope and then scanned to produce a topographical map of the area containing the cantilever. A second higher resolution scan was produced of the area immediately around the microcantilever, allowing the indenter tip to be placed close to the free end of the microcantilever and the cantilever to be loaded. For measuring elastic properties, multiple loadings were performed at decreasing distances from the fixed end of each cantilever, at a constant strain rate of 6x10^{-5}s^{-1} to displacements of 200nm. To measure size effects in yield stress each cantilever was loaded once at a rate of 5nm{s^{-1}}; depending on the cantilever size the target displacement was set between 400nm and 3μm to ensure that yielding occurred. For measuring fracture toughness of grain boundaries a single displacement of each cantilever was carried out at a strain rate of 6x10^{-5}s^{-1} until fracture occurred or the displacement reached 1000nm. Following testing each cantilever was imaged in the SEM to allow the effective cantilever length (i.e. the distance between the loading point and fixed end) to be measured.
DISCUSSION

Single Crystal Elastic Properties in Polycrystalline copper

The cantilevers tested were analyzed using the methodology outlined in [5]. In summary it was found that for beams with an aspect ratio (length from loading point to fixed end, L: width) greater than 6, simple encastre beam behavior was followed, so that:

\[ S = \frac{\delta}{P} = \frac{L^3}{3EI} \] (1)

Here \( S \) is the measured compliance (the ratio between displacement, \( \delta \), and load, \( P \)), \( E \) is the Young’s modulus along the length of the beam and \( I \) is the beam’s second moment of area. Young’s modulus was calculated from the gradient of plots of \( L^3 \) versus \( S \). The expected value of Young’s modulus for a given orientation was also calculated from single crystal elastic constants in the literature [8] using the relationship:

\[ \frac{1}{E_{\text{av}}} = \frac{c_{11} + c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} - 2\left(\frac{1}{c_{11} - c_{12}} - \frac{1}{2c_{44}}\right)(w^2v^2 + v^2w^2 + w^2u^2) \] (2)

Table 1 summarizes the values measured for the cantilevers of orientation \([uvw]\) manufactured inside single grains with surface plane \((hkl)\) and the literature-derived values of \( E \).

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>[uvw]</th>
<th>Experimentally measured Modulus (GPa)</th>
<th>Modulus range derived from Literature values (GPa)</th>
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<tr>
<td>8 13 23</td>
<td>11 5 1</td>
<td>87</td>
<td>85-103</td>
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<tr>
<td>8 13 23</td>
<td>11 5 1</td>
<td>79</td>
<td>85-103</td>
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<tr>
<td>7 8 9</td>
<td>15 12 1</td>
<td>131</td>
<td>116-134</td>
</tr>
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Table 1: Values of Young’s modulus both experimentally measured using microcantilevers and derived from the literature values of elastic constants.

The experimentally measured values are in good agreement with those derived from literature values for single crystal Young’s Modulus.

Yield Stress Size Effects in Single Crystal Copper

Each load-displacement curve was converted to a stress-strain curve using simple beam theory. The maximum stress (at the lower surface at the beam root) in a triangular cantilever loaded in the elastic regime is:

\[ \sigma_{\text{max}} = \frac{24P}{h^2} \] (3)

and the maximum strain is:

\[ \varepsilon_{\text{max}} = \frac{2h\delta}{L^2} \] (4)

Where \( P = \text{load} \), \( L = \text{effective beam length} \), \( a = \text{beam width} \), \( h = \text{beam thickness} \) and \( \delta = \text{displacement} \).