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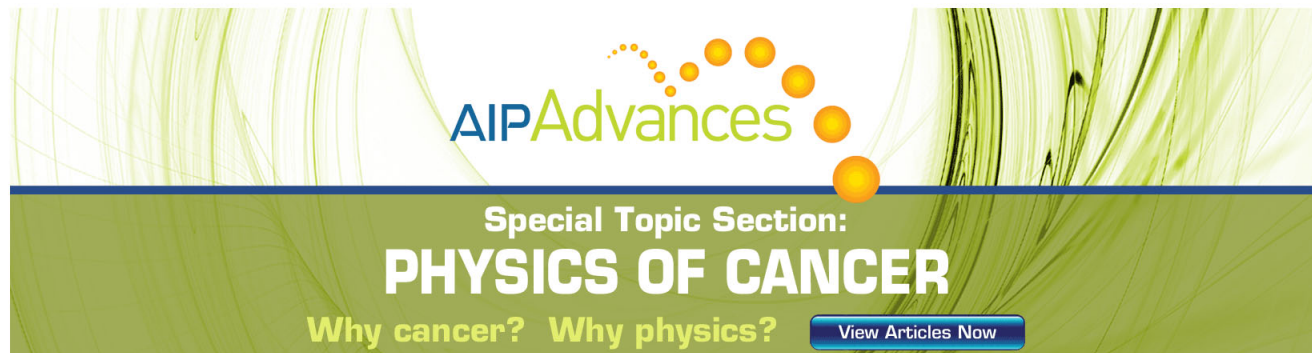
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Impurity-free seeded crystallization of amorphous silicon by nanoindentation

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We demonstrate that nanoindents formed in amorphous Si films, with dimensions as small as ~ 20 nm, provide a means to seed solid phase crystallization. During post-indentation annealing at $\sim 600^\circ\text{C}$, solid phase crystallization initiates from the indented sites, effectively removing the incubation time for random nucleation in the absence of seeds. The seeded crystallization is studied by optical microscopy, cross-sectional transmission electron microscopy, and electrical characterization via Hall measurements. Full crystallization can be achieved, with improved electrical characteristics attributed to the improved microstructure, using a lower thermal budget. The process is metal contaminant free and allows for selective area crystallization. © 2011 American Institute of Physics. [doi:10.1063/1.3647587]

INTRODUCTION

Polycrystalline silicon (poly-Si) is technologically important in a range of applications from CMOS integrated circuits to large area electronics such as solar cells and thin-film-transistor based devices.^{1–6} An important area of study is the crystallization of relatively low-cost a-Si to form high quality poly-Si (Refs. 1 and 5–11). Generally, a low-temperature process is desirable and the final microstructure should be composed of large, defect-free grains, with the aim of achieving high carrier mobility and lifetime. Mechanisms for selective area crystallization are also desirable.^{12–14} A number of techniques to achieve these attributes have been studied, such as laser crystallization processes^{13,14} and various metal-induced solid phase crystallization schemes.^{15,16}

Nanoindentation-induced phase transformations of crystalline Si have been extensively studied and more recently these studies have been extended to a-Si.^{17–21} During nanoindentation loading, a-Si transforms to a metallic phase (Si-II) at a pressure of ~ 11 GPa. During unloading this phase, further phase transforms to either a polycrystalline mixture of high pressure phases (Si-III and Si-XII) or a-Si, depending on the rate of unloading. The indent size also determines the formation of the crystalline phases as they are believed to form through a nucleation and growth process. Hence, slower unloading with a larger indent size promotes the formation of these phases. Thus, under appropriate loading/unloading conditions, a nano- to microscale zone of crystalline Si (Si-III/Si-XII) can be formed in an a-Si matrix. These high pressure crystalline phases formed during the indentation have the ability to further phase transform to normal diamond-cubic poly-Si at annealing temperatures as low as 150°C .^{22,23} It is interesting then to examine whether the phase transformed zones can be used to seed and enhance

the solid phase crystallization of a-Si. In this study, we investigate the use of nanoindentation to seed solid phase crystallization of thin a-Si films formed by ion-implantation of silicon-on-insulator (SOI) wafers. We investigate the nucleation and growth of poly-Si from the nanoindented sites during subsequent thermal annealing and measure the electrical properties of films formed using this seeded crystallization.

EXPERIMENT

Amorphous silicon films were formed by Si ion-implantation of SOI wafers. The wafers were composed of a 180 nm Si(100) p-type (doped with a background concentration of boron to a resistivity of $14\text{--}22\ \Omega\ \text{cm}$) layer on a 200 nm SiO₂ layer on a Si(100) wafer. Implantation of Si at energies of 50 and 100 keV to fluences of 1×10^{15} and $5 \times 10^{15}\ \text{cm}^{-2}$, respectively, was performed at -170°C to completely amorphize the top Si layer. Samples were annealed at 450°C for 30 min to convert the a-Si to a relaxed state which is usually required to induce phase transformations during indentation.¹⁸

Indentation was performed under various conditions, using a Hysitron Triboindenter fitted with a Berkovich tip, to form indents ranging from < 20 nm to approximately 600 nm in diameter. The corresponding phase transformed zones extend from the surface to depths ranging from ~ 20 nm to the depth of the underlying SiO₂ (180 nm). The unloading rate, which determines the final composition of the indent,^{17–19} was varied such that indents containing mostly high pressure crystalline Si phases (Si-III/Si-XII) with none or little a-Si were formed in addition to indents expected to be composed almost entirely of a-Si.

Samples were furnace annealed at $600\text{--}625^\circ\text{C}$ for various times. These temperatures were chosen to allow full crystallization of the a-Si films in time periods ranging from minutes to hours. Optical microscopy allowed observation of the growth of crystalline regions in the a-Si film. Raman

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micro-spectroscopy was performed on residual indents to assess the composition of the phase transformed zones. Measurements were made using a Renishaw 2000 system fitted with a 632 nm wavelength laser which could be focused to a spot of $\sim 1 \mu\text{m}$ diameter. Cross-sectional transmission electron microscopy (XTEM) samples were made from selected indents by a focused ion beam milling process that has been described elsewhere.²⁴ The technique routinely allows site-specific cross-sections to be made on features larger than $\sim 200 \text{ nm}$. Imaging was performed using a Philips CM 300 transmission electron microscope.

Hall measurements were performed on selected fully crystallized samples to extract the carrier transport properties of the resultant poly-Si. For these measurements, the starting a-Si was implanted with boron to a sheet concentration of $1 \times 10^{15} \text{ cm}^{-2}$ to facilitate straightforward electrical contacts to be made to the p^+ poly-Si. Van de Pauw mesa structures, with a central region of area $20 \times 20 \mu\text{m}^2$, were fabricated

in the a-Si films. Indentation was then performed over the central region of the structures to induce seeded crystallization during subsequent annealing. Measurements were made using an Accent HL5500PC Hall effect measurement system.

RESULTS

Figure 1 shows two arrays of nanoindents formed in a-Si after annealing at 625°C for 30 min. The maximum load was incremented from $100 \mu\text{N}$ up to 10 mN over the array of 64 indents. The resulting indents range in dimension from $\sim 20 \text{ nm}$ to $\sim 600 \text{ nm}$, thus allowing investigation of the effect of indent size on the seeding. Loading and unloading was performed “slowly” (0.17 mN/s) or “fast” (10 mN/s). High pressure crystalline phases could only be detected by Raman in the largest indents made at the slow unloading rate (in agreement with a previous study²⁵). However, all indents act as nucleation sites for crystallization with the exception of the two smallest indents for both unloading rates.

Figure 2 shows optical images of the indented central region of one of the Van de Pauw mesa structures at various anneal times during a 600°C anneal. Preferential seeded crystallization is clearly evident with the indented region fully recrystallized after 2 h. An unseeded a-Si region is shown for comparison after the 2 h anneal, where only a few isolated spots of material have crystallized and the film remains mostly a-Si. Even after a further 2 h of annealing, the unseeded film is still not completely crystallized. Table I summarizes the electrical measurements made on the Hall structures. The seeded poly-Si film (which is crystallized in shorter times) has approximately ten times lower resistivity, higher dopant activation, and approximately six times higher carrier mobility than the unseeded poly-Si.

Figure 3 shows XTEM images taken from a selected indent after annealing for 30 min at 625°C (sample shown in

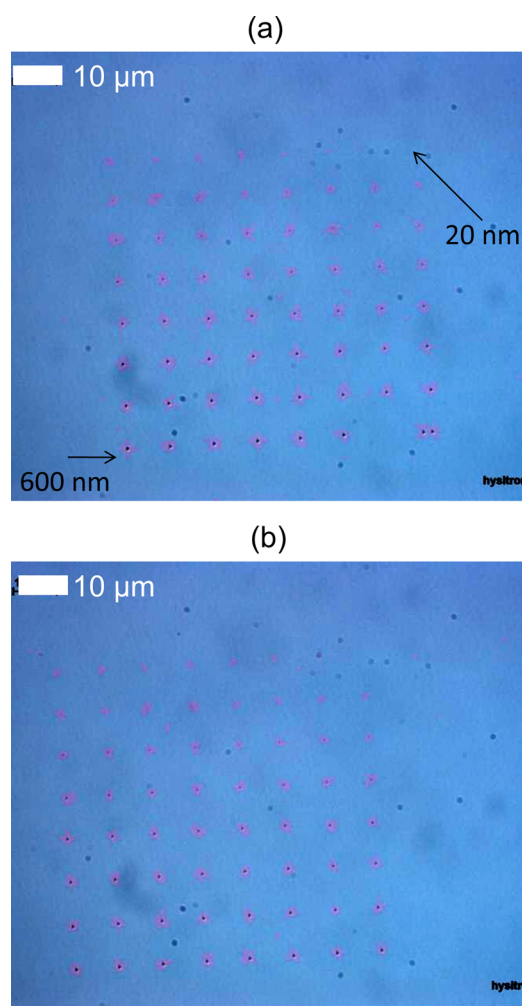


FIG. 1. (Color online) Optical microscope images of nanoindents made in relaxed a-Si following annealing at 625°C for 30 min. Arrays of 64 indents (8×8) were made with the maximum indentation load being incremented with each indent to form a range of sizes. The smallest and largest diameters are labeled in (a). Unloading was performed (a) slowly (0.17 mN/s) or (b) rapidly (10 mN/s). Crystallized regions (lighter contrast) around each indent are observable (the a-Si is darker contrast). The radius of each zone decreases with decreasing indent size. Seeding is clearly observed for all indents except for the first two (smallest) in each array.

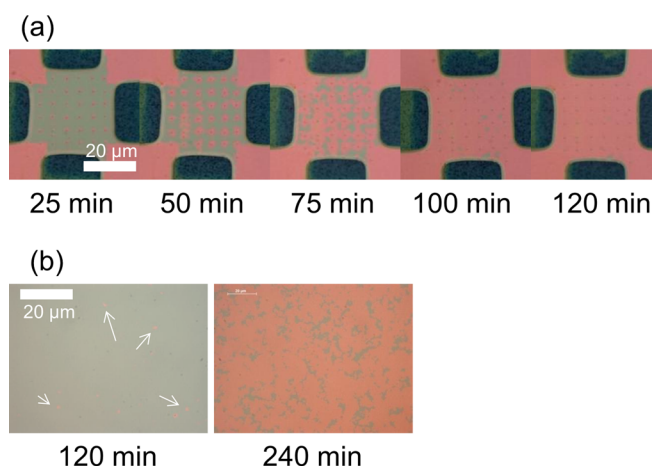


FIG. 2. (Color online) Optical microscope images of amorphous Si regions during thermal annealing at 600°C . The central region of a Hall mesa structure is shown in (a). The green coloured region is a-Si and has been indented with an array of indents separated by $5 \mu\text{m}$. During annealing, the seeding from these sites is clearly visible and the region is fully crystallized after 2 h. An unindented a-Si region away from the Hall pattern is shown in (b). After annealing for 2 h, only a few random crystallized regions are visible in still a mostly a-Si region (marked with arrows as they are difficult to see). Even after annealing for 4 h, the film is not fully crystallized.

TABLE I. Summary of the electrical measurements made on the seeded and unseeded annealed films following annealing at 600 °C. Also included are unseeded films annealed at higher temperatures and longer times.

Sample	Sheet resistivity (Ω/sq)	Hole mobility ($\text{cm}^2/\text{V s}$)	Sheet carrier concentration (cm^{-2})
Unindented	Highly resistive (not crystallized)		
Indented	490	26.1	4.9×10^{14}
Unindented (600 °C for 300 min)	4440	4.2	3.3×10^{14}
Unindented (625 °C for 60 min)	4230	4.3	3.4×10^{14}

Figure 1 with crystallized zones surrounding each indent). This is one of the larger indents and crystalline material in the indented zone (formed by phase transformations) is visible. The sample has been annealed at 625 °C so all crystalline material is the Si-I phase. The grain size in the indented zone (Fig. 3(b)) is typical of what has been observed previously for phase transformed zones with grains being smaller than 100 nm. However, the poly-Si material grown during the subsequent annealing surrounding the phase transformed zone and seeded by the indent site is composed of grains of greater than 1 μm in lateral dimension and extending from the surface to the underlying SiO_2 as shown in Fig. 3(c). These initial analyses also indicate that the grains are aligned with each other, presumably because the grains of Si-III/Si-XII formed by indentation are preferentially aligned^{17,18} and will retain this as they transform to Si-I during annealing.^{22,23}

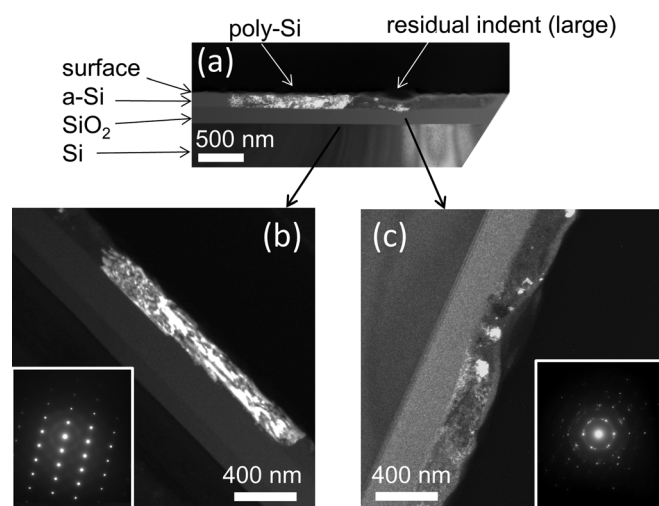


FIG. 3. XTEM images from a selected nanoindent made in the relaxed a-Si film and annealed for 30 min at 625 °C. This is one of the larger indents (~500 nm in diameter) as it is prohibitively difficult to form a foil containing a sub 100 nm indent. Part (a) shows a low magnification dark field image of the cross-section through the indent. The crystallized region around in the indent is clearly visible in the top 180 nm a-Si layer. Part (b) shows a similar dark-field image of one of the crystals formed in the crystallized zone around the indent. These grains are generally >1 μm in dimension and span from the surface to the underlying SiO_2 layer. The inset shows the selected area diffraction pattern (SADP) from one of these grains and confirms the single crystal structure. Part (c) is a dark field image highlighting some of the grains formed by the phase transformation itself. These are all less than 100 nm in diameter. The inset shows the SADP from the zone which is polycrystalline.

DISCUSSION

These results clearly show preferential seeded crystallization of a-Si via nanoindentation and illustrate how the nanoindents act as nucleation sites. We first discuss some likely mechanisms that could drive the observed seeding effect. First, it is well known that some metallic species, such as Ni and Al, enhance solid phase crystallization of a-Si.^{7,15,16} Indeed, this phenomenon has been exploited in formation of high quality poly-Si for solar and thin-film-transistor applications. Recently, Asano *et al.*^{26–28} demonstrated seeded crystallization via transfer of Ni through nanoimprinting to selected locations in an a-Si film followed by thermal annealing. In the present study, we tested whether metal impurities are playing a role by re-implanting indented samples under the initial amorphization conditions prior to annealing (results not shown here). However, no seeding was observed after re-amorphization and crystallization was observed to occur through the normal random nucleation and growth mechanism. Thus, if trace amounts of Ni or Al are transferred during indentation, they are not at high enough levels to enhance the crystallization at the indented sites. In addition, this same experiment confirms that the topographical changes to the sample surface, induced by the indentation, do not provide seeding sites for the crystallization since the re-amorphization is not expected to induce any significant changes to the shape of the residual indents. Hence, these results suggest that it is the phase transformations or structure modifications induced by indentation that results in the seeded crystallization.

For larger indents, significant volumes of high pressure crystalline Si phases are formed and these are visible in Raman spectra taken from the indents. These phases are also clearly observed by XTEM (Fig. 3). The authors have shown previously that volumes of Si-III/Si-XII in residual indents, that are metastable at room temperature, transform to polycrystalline Si-I during low temperature annealing ($T < 300^\circ\text{C}$).^{22,23} These small zones of poly-Si can clearly act as seed crystals for subsequent crystallization. Indeed, this behavior is observed in the XTEM images (Fig. 3). However, for the smaller indents (<500 nm), it is less obvious that high pressure crystalline phases are formed during nanoindentation. The formation of the Si-III/Si-XII during unloading is nucleation limited. Thus, small indents and rapid unloading promote the transformation to a-Si rather than Si-III/Si-XII. Under previous rapid unloading studies under the conditions used in the current study, we did not observe Si-III/Si-XII by Raman micro-spectroscopy and have only rarely seen small crystallites (~10 nm) of Si-III/Si-XII in large phase transformed zones by XTEM.¹⁹ In summary, for the sub-500 nm indents, we have seen no previous evidence for the formation of Si-III and Si-XII in load/unload curves, Raman, and XTEM. However, the fact that the seeding effect is still observed for small nanoindents made in relaxed a-Si suggests that it is possible that either small volumes (below the detection limit of Raman) of nanocrystals of Si-III/Si-XII exist in these phase transformed zones or that the pressure-induced form of a-Si that results from indentation can also preferentially seed poly-Si

compared to normal ion-implanted a-Si. It has been shown in another study that the structure of nanoindentation-induced a-Si does differ from that of ion-implanted a-Si.²⁹ Further work and experimental development is required to investigate this.

Since the indentation provides seeds for subsequent solid phase crystallization, it effectively eliminates the initial incubation period observed for unseeded solid phase crystallization. Although the rate of crystallization with and without seeding may be the same, the initial change in the nucleation kinetics will result in changes in the final microstructure of the crystallized film. In addition to the post-indent annealing conditions and the volume of Si-III/Si-XII formed within the indentation zone itself, the final microstructure of the crystallized Si should be controlled by the pattern of indents or nucleation sites (indent positions and spacing). Hence, the nucleation sites are limited to the number of indents made, which are separated by 5 or 10 μm in this study. The number of nucleation sites in an unseeded region of the same area will depend on the initial preparation conditions (deposition conditions, implantation conditions, concentration of impurities) of the a-Si and the annealing temperature. However, we suggest that the number of nucleation sites generated by random nucleation per unit area is considerably larger than that induced by the indentation patterns used in the present study. Therefore, the average grain size is smaller for the random nucleation case, resulting in higher resistivity films (see electrical measurements in Table I). A more detailed study confirms this for a range of ion-implanted a-Si films annealed in the temperature range 600 to 650 °C.³⁰ Finally, the number of indents on the Hall structure was chosen arbitrarily in this case and, in principle, under the correct annealing conditions, the film could have been fully crystallized by seeding from a single indent site or sparsely separated indents. We suggest that this may result in the optimum microstructure. Further work is required to fully explore this proposal.

CONCLUSION

We have shown that nanoindentation of a-Si provides seeding sites for solid phase crystallization during thermal annealing. This allows full crystallization of an a-Si film to polycrystalline Si with a lower thermal budget than an unseeded process. The seeding is metal-free thereby eliminating contamination from metallic species in the poly-Si material. Furthermore, by performing indentation at specific sites or over specific areas, selected area crystallization can be achieved.

The directed nucleation and growth of polycrystalline Si results in a more favourable microstructure (larger grain size) when compared to the unseeded crystallization that occurs via a random nucleation and solid phase crystallization process. This is observed in the initial TEM studies performed here and the electrical measurements of seeded poly-Si films. For example, a boron doped poly-Si film formed by indentation seeding and thermal annealing exhibits a sheet resistivity which is an order of magnitude lower than an unseeded film annealed at the same temperature

(600 °C). Furthermore, the measured hole mobility is 6 times lower.

Finally, nanoindentation-seeded crystallization is shown to be a potentially attractive approach to forming poly-Si from a-Si films for use in solar cells and thin-film-transistor based devices. The process is also scalable by adapting the technique to larger scale nano-imprint stamp technology.

ACKNOWLEDGMENTS

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