In situ Raman characterization of reversible phase transition in stress-induced amorphous silicon

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(Received 8 July 2007; accepted 15 August 2007; published online 4 September 2007)

The authors report a reversible phase transition of stress-induced amorphous silicon subjected to laser heating. In situ Raman characterization suggested that a metastable crystalline phase precipitates from the amorphous silicon upon annealing at \(-400^\circ\text{C}\) and vanishes after subsequent cooling at room temperature. The unusual reversible phase transition is most likely associated with the unique atomic structure of stress-induced amorphous silicon and high residual stresses within amorphous imprints. © 2007 American Institute of Physics. [DOI: 10.1063/1.2779933]

Amorphous silicon (a-Si) has been widely used in high-performance solar cells and neutron detectors. Unlike the crystalline polymorphs of silicon, the atomic configuration of a-Si strongly depends on preparation methods, although it is generally described as a random tetrahedral network. For example, the structure and properties of a-Si prepared by chemical vapor deposition (CVD) is largely affected by the incorporation of hydrogen (the so-called a-Si:H), and small ordered silicon domains (<2 nm) can exist in CVD-grown a-Si under some growth conditions. Amorphous Si can also be produced by high pressures and this stress-induced amorphous phase was reported to contain a large number of ordered clusters. In the past few years, much attention has been paid to the structural relaxation and crystallization of a-Si with the aim to optimize its structure for device applications at elevated temperatures. Nanocrystalline cubic Si (c-Si) has been obtained by annealing a-Si at the temperatures ranging from 500 to 1000 °C. However, the thermal stability of stress-induced a-Si in a wide temperature range, particularly at low heating temperatures, remains to be comprehensively illuminated.

Raman spectroscopy is an ideal tool for studying the phase transitions of a-Si because the major bands of a-Si are Raman active. The structural parameters including the mean bond-angle distortion Δθ can be easily determined from the full width at half maximum (FWHM) \(\Gamma\) of its transverse optical (TO) band using the empirical equation \(\Gamma = 15 + 6\Delta \theta\). In this letter, we outline a systematic in situ Raman investigation of a reversible phase transition in a stress-induced a-Si at low heating temperatures, which has not been reported before.

Amorphous silicon was produced on a (111)-oriented silicon wafer by a Vickers-type microindentation. The Amorphous imprints were generated by loading 0.1 N force in 1 s, keeping for 15 s, and then retracting in 1 s. The residual indents are about 3 μm in the lateral dimensions. Micro-Raman spectra were acquired by a Raman microscope (Renishaw, UK), where an Ar\(^{+}\) laser beam (excitation wavelength of 514.5 nm) was used. The size of the laser spot is about 1 μm in diameter, which gives a power density of ~2500 kW/cm\(^2\) at the laser power of 20 mW. The Lorentzian curve was used for fitting the TO peak of the crystalline silicon and the Gaussian curve was used for other bands.

A typical micro-Raman spectrum acquired from a residual imprint is shown in Fig. 1(a). All the four characteristic bands of a-Si can be identified, including the TO mode at 480 cm\(^{-1}\) with a FWHM of 63 cm\(^{-1}\), LO-like mode at 410 cm\(^{-1}\), LA mode at 290 cm\(^{-1}\), and TA mode at 150 cm\(^{-1}\). This reveals the formation of a-Si by microindentation tests. The distribution of a-Si around a residual indent is imaged by Raman mapping, as shown in the inset in Fig. 1. The mean bond angle distortion of the stress-induced a-Si is estimated to be about 7.5° from the FWHM of the TO band (63 cm\(^{-1}\)), which is located at the smaller end as compared with that (7°–11°) of the a-Si grown by CVD methods. Additionally, the TO mode of c-Si at 520 cm\(^{-1}\) is also presented, which comes from the surrounding silicon substrate.

Laser beam irradiation was employed to heat the a-Si imprints, which favors in situ monitoring of structural changes during annealing. The time required to establish the thermal equilibrium in c-Si is very short (within milliseconds) as estimated from the heating area (~1 μm\(^2\)), the laser power density (2500 kW/cm\(^2\)), the heat conductivity (1.3 W cm\(^{-1}\) K\(^{-1}\)), and the heat capacity (800 J kg\(^{-1}\) K\(^{-1}\)) of c-Si. For a-Si, the time for thermal equilibrium may be longer due to its poorer heat conductivity, but should still be negligible as compared to the time to acquire a typical Raman spectrum (30 s). Therefore, the temperature of the surfaces irradiated by the laser beam can be monotonically determined through measuring the TO band shift of Si (Ref. 13) and the Stokes/anti-Stokes intensity ratio \(I_{S}/I_{A}\). For the crystalline Si matrix, there is virtually no temperature increase during Raman scanning with a power of 20 mW, as judged from the unchanged TO peak position (for comparison, Raman spectrum taken from c-Si heated by a temperature-programmed sample cell shows significant peak shift at the temperature as low as 50 °C). For a-Si, an obvious temperature raise is evidenced by the low frequency shift of its TO band in the Raman spectra taken at different laser powers [see Fig. 1(b)]. From the shift (~10 cm\(^{-1}\)) of the a-Si TO peak at the laser power of 20 mW, the corresponding temperature is ~400 °C with an assumption of a similar temperature dependence as c-Si. This value is further confirmed by the Stokes/anti-Stokes intensity measurements, as will be discussed later.

An amorphous microindent was continuously irradiated by a 514 nm Ar\(^{+}\) laser with a power of 20 mW, and the Raman spectra were recorded every 30 s, as shown in Fig. 2(a). After annealing for ~6 min, a peak emerges at about...
510 cm\(^{-1}\) and quickly grows as the strongest band in the Raman spectra. Significantly, the position shifts of the \(a\)-Si TO peak at about 470 cm\(^{-1}\) and \(c\)-Si at 520 cm\(^{-1}\) have not been seen, indicating a near equilibrium temperature during the continuous laser irradiation. Thus, the peak should not come from the temperature-induced \(c\)-Si TO band shift, but rather a crystalline phase precipitates from \(a\)-Si during the low temperature annealing. The formation of the phase during laser annealing can be seen more clearly from the spectra after background subtraction [see Fig. 2(b)]. All the Raman spectra were subtracted by the initial spectrum of \(a\)-Si. The first five spectra, corresponding to the incubation period of the phase transition, are featureless. Subsequently, an asymmetric peak located at 510 cm\(^{-1}\) gradually shows up with annealing. Meanwhile, the \(c\)-Si TO band is completely deducted. The disappearance of the \(c\)-Si peak in the subtracted spectra further confirms that no peak shift and intensity change occur in the crystalline substrate during laser annealing. In addition to the major peak at 510 cm\(^{-1}\), a small shoulder peak at \(\sim 494\) cm\(^{-1}\) also becomes evident [Fig. 2(b)]. The phase appears to be the wurtzite Si IV because the features of its spectrum, an asymmetric peak at 510 cm\(^{-1}\) with broadening in the low-wave-number side and a small shoulder at \(\sim 494\) cm\(^{-1}\), are well consistent with those of Si IV\(^{15-17}\). In particular, the weak shoulder peak at 494 cm\(^{-1}\) is the unique characteristic of Si IV, which distinguishes it from the very similar Raman spectrum of nanocrystalline \(c\)-Si. The formation temperature of the Si IV phase was determined by measuring the Stokes and anti-Stokes components of Raman spectrum, as shown in Fig. 3. The anti-Stokes/Stokes intensity ratio \((I_A/I_S)\) of the Si IV peak at 510 cm\(^{-1}\) is \(\sim 0.339\). According to the equation\(^{14}\) \(I_A/I_S=\exp(-\hbar\omega_0/KT)\), the annealing temperature is \(\sim 408^\circ C\), which is fairly consistent with the temperature \(\left(400^\circ C\right)\) estimated by \(a\)-Si TO peak shift at the laser power of 20 mW, as shown in the inset of Fig. 1(b).

Surprisingly, when the annealed samples were cooled at room temperature, the Si IV peak at 510 cm\(^{-1}\) gradually disappears (Fig. 4). To keep the samples cooling at room temperature, we performed Raman measurements at 5 min intervals instead of 30 s, during which the laser beam was blocked. The gradual intensity attenuation of the 510 cm\(^{-1}\) peak occurs with cooling and the peak completely disappears after \(\sim 30\) min. The fading of the peak was also observed by reducing laser powers, but peak shift takes place because of the decrease of the instant temperatures caused by laser heating during Raman scanning. The cycle with 510 cm\(^{-1}\) peak emerging on annealing at \(\sim 400^\circ C\) and vanishing on cooling...
at room temperature can be reproduced many times, suggesting that the phase transition is reversible.

It has been reported that α-Si transforms into nanocrystalline c-Si at the temperatures ranging from 500 to 1000 °C, and the TO peak of nanocrystalline c-Si shows a significant shift to a lower wave number from the bulk band at 520 cm⁻¹ due to the quantum confinement effect. At a first glance, one may consider the present observations as an evidence of the formation of nanocrystalline Si. However, this possibility appears to be questionable because of the following reasons. First, the annealing temperature in our experiments is only ~400 °C, not high enough for the formation of nanocrystalline c-Si. Second, nanocrystalline c-Si is thermodynamically stable and should not disappear upon cooling at room temperature. Particularly, in order to produce similar spectra, as shown in Fig. 2(b), the size of the c-Si nanocrystals is ~10 nm, which is definitely large enough to be maintained at room temperature.

The phase transition during laser heating appears natural because the transition from an amorphous phase to a crystalline one is thermodynamically favorable. The formation of the metastable Si IV has been observed during low-temperature annealing at ~200 °C. The appearance of Si IV at low temperature is thought to be related to the atomic configuration of α-Si, which has been suggested to contain a large number of Si IV clusters. Recent high resolution electron microscopy observations also demonstrated the existence of a high density of crystal-like clusters in α-Si produced by microindentation. Moreover, the coprecipitation of Si IV and α-Si from Si II/Si VII as suggested by recent Raman investigations indicates that the two metastable phases, α-Si and Si IV, have similar formation energies and the energy barrier for the transition between them should be very small. Upon laser annealing, these wurtzite Si IV clusters may act as the embryos for the formation of nanosized metastable phase, leading to the emergence of the corresponding peaks in the Raman spectra. However, the vanishing of the metastable Si IV phase upon cooling at room temperature, which suggests that the Si IV phase is not stable at room temperature, is difficult to explain because it looks inconsistent with thermodynamics. Two factors may cause the instability of the crystalline phase as outlined below. Because of the low annealing temperature during the formation of the Si IV phase, the crystalline nuclei may not be able to grow to a size larger than the critical size that the crystals can thermodynamically survive at low temperatures. Another factor that may induce the room-temperature reaction is the high residual stresses within the microindents. It has been reported that the residual stress caused by inhomogeneous deformation within the microindents is about a few gigapascals (Ref. 23), which may be high enough to promote the transition from Si IV to α-Si.

In summary, a reversible phase transition was found in stress-induced α-Si subjected to laser annealing and subsequent cooling at room temperature. Our results suggest that the transition is probably associated with the appearance and vanishing of the metastable Si IV phase with a nanoscale size. The phenomenon will be helpful for understanding the low-temperature thermal stability and the atomic structure of stress-induced α-Si, and potential device applications utilizing the reversible transition may be expected.