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Nanoindentation Behaviour and Microstructural Evolution of Annealed Single-Crystal Silicon

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***Abstract*—**The nanoindentation behaviour and phase transformation of annealed single-crystal silicon wafers are examined. The silicon specimens are annealed at temperatures of 250, 350 and 450ºC, respectively, for 15 minutes and are then indented to maximum loads of 30, 50 and 70 mN. The phase changes induced in the indented specimens are observed using transmission electron microscopy (TEM) and micro-Raman scattering spectroscopy (RSS). For all annealing temperatures, an elbow feature is observed in the unloading curve following indentation to a maximum load of 30 mN. Under higher loads of 50 mN and 70 mN, respectively, the elbow feature is replaced by a pop-out event. The elbow feature reveals a complete amorphous phase transformation within the indented zone, whereas the pop-out event indicates the formation of Si XII and Si III phases. The experimental results show that the formation of these crystalline silicon phases increases with an increasing annealing temperature and indentation load. The hardness and Young's modulus both decrease as the annealing temperature and indentation load are increased.

***Keywords*—**Nanoindentation, silicon, phase transformation, amorphous, annealing.

I. INTRODUCTION

SILICON is not only a dominant substrate material for the fabrication of microelectronic and mechanical components, but also an important infrared optical material due to the high selectivity of its dielectric characteristics [1]. As a result, the mechanical properties of silicon are of significant interest; most particularly the phase transformations which occur under high pressure loading and on subsequent pressure release. The mechanical properties of bulk silicon are generally evaluated by means of nanoindentation tests. The hardness and Young's properties of the indented specimens are obtained from the resulting load-depth curves using either the Oliver-Pharr method [2] or the work-of-indentation method [3]. Many studies have shown that a discontinuity ("pop-in") event commonly occurs in the loading curve, while another discontinuity ("elbow" or "pop-out") often occurs in the unloading curve [4]. These discontinuities have been widely attributed to phase changes and associated volume and density changes under the indenter.

Many studies have shown that silicon undergoes phase transformation under indentation [5]. At atmospheric pressure, silicon has a cubic diamond structure (Si-I). However, at hydrostatic pressures of 11.2~12 GPa, this diamond structure transforms to a metallic β-tin structure (Si-II) [4]. Moreover, during pressure release, the Si-II transforms into various metastable phases depending on the load release conditions. For example, during rapid unloading, the Si-II phase transforms into amorphous silicon (a-Si). Molecular dynamics simulations have shown that a transformation from β -tin phase to amorphous Si phase may occur even if the indenter radius is only a few nanometers [6]. During slow unloading, the Si-II phase transforms initially to a rhombohedral structure, *r*8 (Si-XII) [7]. However, on further unloading, a reversible transition from Si-XII to body-centred-cubic Si-III phase occurs; resulting in a mixture of Si-XII and Si-III at ambient pressure [7]. The present study performs an experimental investigation into the nanoindentation behaviour and phase transformation of single-crystal silicon wafers annealed at temperatures of 250, 350 and 450ºC, respectively, and then indented to maximum loads of 30, 50 and 70 mN.

II. EXPERIMENTAL PROCEDURE

The nanoindentation tests were performed using device grade p-type single-crystal silicon wafers with a (100) orientation and a thickness of 0.725 mm. Prior to the indentation tests, the specimens were annealed at temperatures of 250, 350 and 450ºC for 15 minutes in an induction furnace. The nanoindentation tests were performed at room temperature in air using an MTS nano Indenter XP system fitted with a Berkovich diamond pyramid tip with a radius of 20 nm. The annealed specimens were indented to three different maximum loads, i.e., 30 mN, 50 mN and 70 mN, respectively. The loading-unloading cycle involved three steps, namely (1) loading to the designated maximum load; (2) holding at this load for 1 s; and (3) smoothly unloading over a period of 10 s. Five separate indentation tests were performed for each experimental condition. The hardness and Young's modulus of the samples were then calculated from the load-displacement curves using the Oliver and Pharr method [2].

Following the indentation tests, thin foil specimens for TEM inspection were prepared using an FEI Nova 200 focused ion beam (FIB) milling system. The cross-sectional microstructures of the various specimens were observed using a Philips Tecnai F30 Field Emission Gun Transmission Microscope with a scanning voltage of 300 keV. In addition, the nature of the amorphous and crystalline phases formed within the indented zones of the different specimens was identified using micro-Raman scattering spectroscopy (RSS) with an average laser spot size of approximately 1 µm.

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III. Results and Discussions

A. Loading-Unloading Curves and Hardness and Young's Modulus Properties

Fig. 1 (a) shows the load-displacement curves of the Si specimens annealed at a temperature of 250ºC and then indented to maximum loads of 30, 50 and 70 mN, respectively. Comparing the three curves, it is evident that all of the loading curves have a smooth, continuous profile with no discontinuities (i.e., pop-in events). However, notable differences are observed in the three unloading curves. For example, in the specimen indented to a maximum load of 30 mN, the unloading curve exhibits an elbow feature (i.e., a gradual change in slope), which indicates a transformation froma diamond cubic structure (Si-I) to an amorphous structure. By contrast, for the specimens indented to maximum indentation loads of 50 mN and 70 mN, respectively, a well-defined pop-out event is observed. The pop-out feature suggests the occurrence of phase transformation from a diamond cubic structure, i.e., Si-I, to a mixture of Si-XII/Si-III crystalline phases.

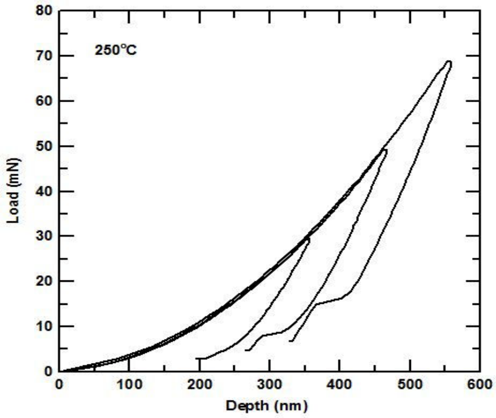
Figs. 1 (b) and (c) show the load-displacement curves of the Si specimens annealed at temperatures of 350ºC and 450ºC, respectively. It is seen that the characteristics of the loading and unloading curves are similar to those of the specimens annealed at a lower temperature of 250ºC, i.e., an elbow feature in the specimen indented to a maximum load of 30 mN, and a pop-out feature in the specimens indented to maximum loads of 50 mN and 70 mN, respectively. Comparing Figs. 1 (a)~(c), it is seen that for the specimens indented under a maximum load of 70 mN, the pop-out load increases with an increasing annealing temperature. However, for the specimens indented to maximum loads of 30 mN and 50 mN, respectively, the pop-out load is independent of the annealing temperature.

As described above, the hardness and Young's modulus values of the annealed specimens were calculated using the Oliver-Pharr method. Table I presents the corresponding results. It is seen that for a given annealing temperature, the hardness and Young's modulus both reduce as the maximum indentation load is increased due to the indentation size effect.

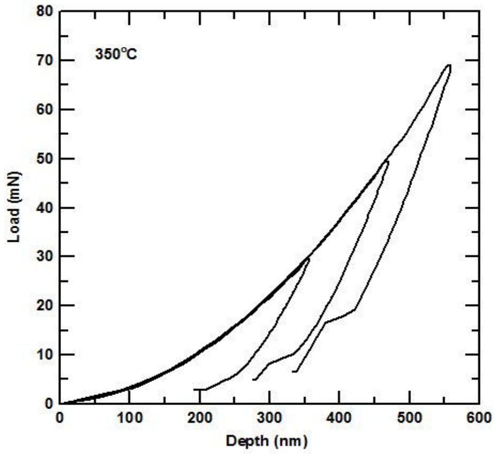
TABLE I
Hardness and Young's Modulus of Annealed Silicon Specimens Indented to Different Maximum Loads

Annealing temperature (ºC)	Load P_{max} (mN)	Hardness (GPa)	Young's modulus
	30	15.99	187.57
250	50	15.52	185.38
	70	15.36	185.16
	30	15.81	184.82
350	50	15.22	184.75
	70	15.08	184.34
	30	15.32	183.86
450	50	15.02	183.52
	70	14.88	183.35

Furthermore, for a constant indentation load, the hardness and Young's modulus decrease with an increasing annealing temperature.



(a)



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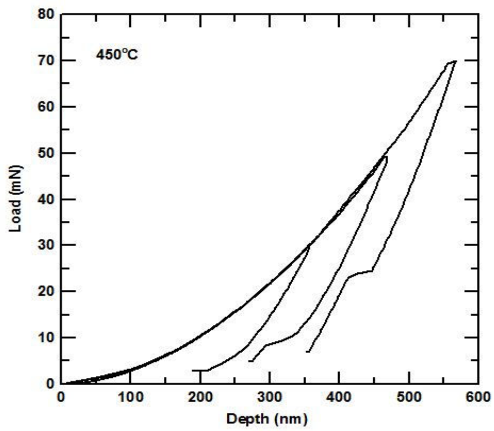


(c)

Fig. 1 Typical load-displacement curves with maximum indentation loads of 30 mN, 50 mN and 70 mN for Si specimens annealed at: (a) 250ºC; (b) 350ºC; and (c) 450ºC

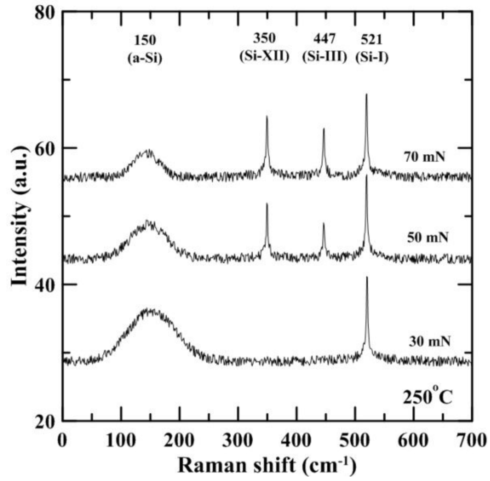
B. Raman Scattering Spectroscopy Analysis

Figs. 2 (a)~(c) show the micro-Raman analysis results for the specimens annealed at temperatures of 250, 350 and 450ºC, respectively, and indented to maximum loads of 30 mN, 50 mN and 70 mN. Fig. 2 (a) shows that for the specimen annealed at 250ºC and indented to 30 mN, the spectrum contains a strong, sharp peak at 521cm^{-1}and a broad peak centred at around 150 cm^{-1}. According to [8], the sharp peak corresponds to pristine Si-I phase, while the broad peak corresponds to a-Si (i.e., amorphous phase). For the specimen annealed at the same temperature of 250ºC but indented to a higher load of 50 mN, the Raman spectrum not only contains the narrow peak at 521cm^{-1}and the broad peak at around 150 cm^{-1}, but also two additional narrow peaks at 350 cm^{-1} and 447 cm^{-1}, respectively. The narrow peak at 350 cm^{-1} indicates the presence of Si-XII, while that at 447 cm^{-1} indicates the presence of Si-III [9]. Under an increased indentation load of 70 mN, the phase peaks associated with a-Si, Si-XII, Si-III and Si-I still remain. However, the intensity of the crystalline phase peaks (Si-XII and Si-III) is slightly diminished, while that of the amorphous phase peak (a-Si) is slightly increased.

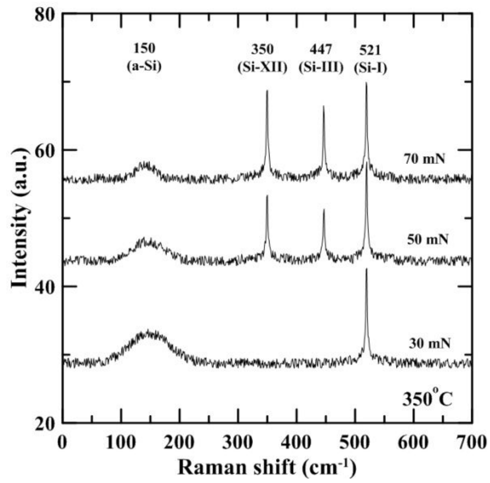
As shown in Figs. 2 (b) and (c), the evolution of the Raman peaks for the specimens annealed at temperatures of 350ºC and 450ºC, respectively, is similar to that of the specimens annealed at 250ºC. Comparing Figs. 2 (a)-(c), it is seen that the intensity of the peaks associated with the Si-XII and Si-III phases increases with an increasing annealing temperature. However, the intensity of the amorphous (a-Si) peak decreases as the annealing temperature is increased. The volume fraction of the a-Si, Si-XII and Si-III phases can be estimated from the relative intensities of the Raman peaks at 150 cm^{-1}, 350 cm^{-1} and 447 cm^{-1}, respectively. Table II presents the volume fractions of the three phases as a function of the peak indentation load (P_{max}) and annealing temperature. For the specimens indented to a maximum load of 30 mN, the deformed microstructure contains only amorphous phase (a-Si), irrespective of the annealing temperature. However, as the annealing temperature and indentation load are increased, the volume fraction of a-Si decreases, while that of Si-XII and Si-III increases.

TABLE II
SUMMARY OF VOLUME FRACTION OF A-SI AND SI III + SI XII PHASE AS A FUNCTION OF PEAK INDENTATION LOAD (PMAX) AND ANNEALING TEMPERATURE

Annealing temperature (ºC)	Load P_{max} (mN)	Volume fraction of phase (%) a-Si	Si III & Si XII
	30	100	0
250	50	78	22
	70	74	26
	30	100	0
350	50	72.4	27.6
	70	68	32
	30	100	0
450	50	70	30
	70	63	37



(a)



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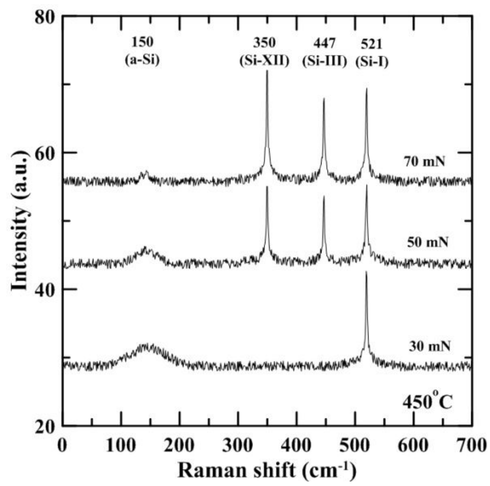

(c)

Fig. 2 Micro-Raman scattering spectroscopy analysis results for Si specimens annealed at: (a) 250ºC; (b) 350ºC; and (c) 450ºC under maximum indentation loads of 30 mN, 50 mN and 70 mN

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C. TEM Analysis

Fig. 3 (a) presents a TEM micrograph of the silicon specimen annealed at a temperature of 250ºC and then indented to a maximum load of 30 mN. It is seen that the indented zone has an approximately triangular shape with a maximum depth of 150 nm. Moreover, a residual indent with a depth of around 45 nm is evident on the specimen surface; indicating the occurrence of significant plastic deformation. Figs. 3 (b) and (c) present high resolution TEM (HRTEM) images of the square regions labeled A and B, respectively, in Fig. 3 (a). Note that the insets in the two figures show the corresponding selected area electron diffraction (SAED) patterns. The SAED patterns diamond structure) phase to a-Si phase (amorphous) phase. Fig. 3 (d) presents the HRTEM results for the square region labeled C in Fig. 3 (a). The results show that the sample retains a perfect diamond cubic single-crystalline structure without phase transformation in the region beyond the indented zone.

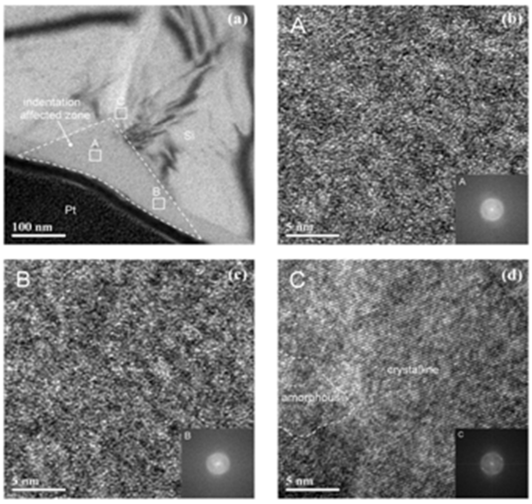

Fig. 3 (a) Cross-sectional TEM micrograph of specimen annealed at 250ºC and then indented to maximum load of 30 mN; (b) HRTEM micrograph of region A in Fig. 3 (a); (c) HRTEM micrograph of region B in Fig. 3 (a); and (d) HRTEM micrograph of region C in Fig. 3 (a)

Fig. 4 presents TEM image of the sample annealed at 250ºC and then indented to a maximum load of 70 mN. It is observed that the indented zone still contains a mixed structure of amorphous phase in the upper region and Si XII or Si III crystalline phase in the lower region. Comparing Figs. 3 (a) and 4 (a), it is seen that given the same annealing temperature (i.e., 250ºC), the amount of amorphous phase decreases with an increasing maximum indentation load, whereas the amount of crystalline Si XII and Si III phase increases. It is noted that this observation is consistent with the volume fraction results presented in Table II.

Fig. 5 presents TEM micrographs of the specimens annealed at 450ºC and then indented to maximum load of 70 mN. Note that for the specimen indented to a maximum load of 30 mN, the indented zone contains only amorphous phase. However, for the specimens indented to maximum loads of 50 mN and 70 mN, the indented zone contains both amorphous phase and Si XII or Si III phase. Comparing Fig. 4 (a) with Fig. 5 (a), it is found that under the same maximum indentation load, the amount of amorphous phase decreases with an increasing annealing temperature, whereas the amount of crystalline Si XII and Si III phase increases. In addition, Fig. 5 (a), corresponding to an annealing temperature of 450ºC and maximum indentation load of 70 mN, show the existence of a crack emanating from the bottom of the indented zone and extending into the silicon substrate. Thus, it is inferred that 70 mN represents the critical load for micro-fracture initiation in the present samples.

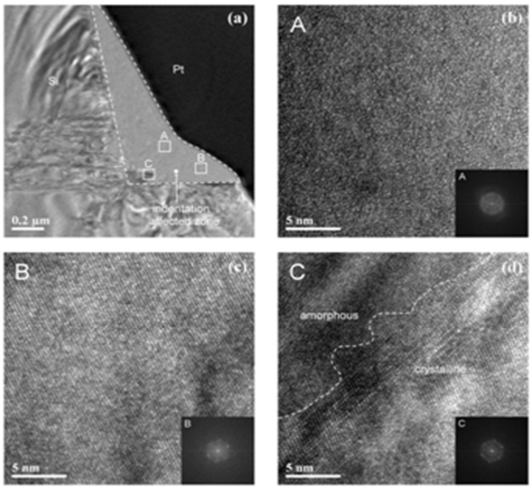

Fig. 4 (a) Cross-sectional TEM micrograph of specimen annealed at 250ºC and then indented to maximum load of 70 mN; (b) HRTEM micrograph of region A in Fig. 4(a); (c) HRTEM micrograph of region B in Fig. 4 (a); and (d) HRTEM micrograph of region C in Fig. 4 (a)

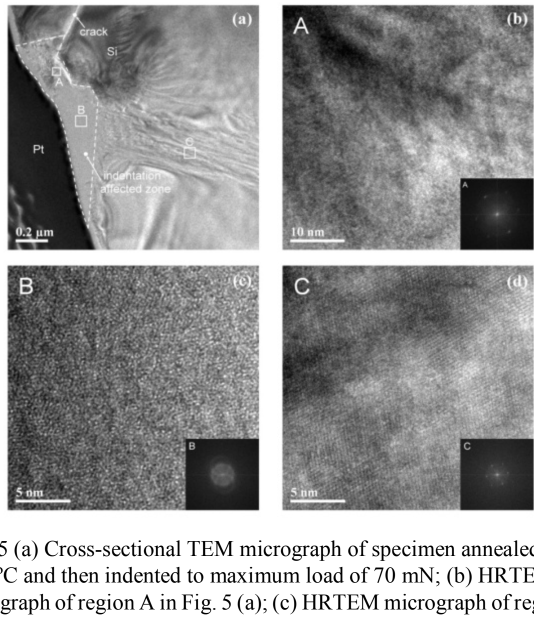

Fig. 5 (a) Cross-sectional TEM micrograph of specimen annealed at 450ºC and then indented to maximum load of 70 mN; (b) HRTEM micrograph of region A in Fig. 5 (a); (c) HRTEM micrograph of region B in Fig. 5 (a); and (d) HRTEM micrograph of region C in Fig. 5 (a)

IV. CONCLUSIONS

This study has investigated the mechanical properties and phase evolution of single-crystal silicon wafers annealed at temperatures ranging from 250~450ºC and then indented to maximum loads of 30, 50 or 70 mN. It has been shown that the unloading curves of the specimens indented to a maximum load of 30 mN exhibit an elbow feature for all values of the annealing temperature, while those of the specimens indented to a maximum load of 50 mN or 70 mN exhibit a pop-out feature. In addition, an Oliver Pharr analysis of the loading-unloading curves has shown that the hardness and Young's modulus of the indented specimens decrease with an increasing annealing temperature and indentation load. The Raman analysis results and TEM observations have revealed that the elbow feature in the unloading curves corresponds to the formation of a-Si (amorphous phase), while the pop-out feature corresponds to the formation of crystalline Si XII and Si III phases. In addition, it has been shown that as the annealing temperature and indentation load increase, the amount of amorphous phase reduces, whereas the amount of crystalline Si XII or Si III phase increases. Finally, the TEM observations have shown that for an annealing temperature of 450ºC and an indentation load of 50 mN or 70 mN, a microcrack initiates in the base of the indented zone and propagates into the underlying silicon substrate.

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