Conducting atomic force microscopy study of phase transformation in silicon nanoindentation

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We report the study of phase transformation in the nanoindentation of Si by conducting atomic force microscopy. Distinctively high current features with a smallest size of around 20 nm have been observed and correspond directly to the generated conductive Si-III and/or Si-XII phases under pressure release. Local current-voltage relationships on the high current sites have also been obtained and found to follow the Fowler-Nordheim tunneling equation. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1780609]

Pressure-induced phase transformation in Si has long been a subject of interest due to the importance of this material. Various phases with distinctive crystalline structures existing at different pressure ranges have already been identified.[1] In indentation experiments, phase transformation details have been obtained from Raman microspectroscopy[2–4] and transmission electron microscopy studies.[4–7] It is known that the atmospheric phase Si-I (diamond structure) undergoes a phase transformation to the Si-II (β-Sn structure) phase upon loading. When the pressure is released, metastable crystalline phases Si-III (bc8 structure) and Si-XII (r8 structure), *a*-Si (amorphous) and untransformed Si-I are found to coexist in the indented region.[2–7] The phase transformation is also accompanied with the discontinuity (also called popout) or/and the elbow effects in the unloading curve. A strong correlation has been found between the discontinuity effect and the appearance of Si-III and Si-XII, while the elbow effect is mainly related to the appearance of *a*-Si.[2]

Since both Si-III and Si-XII have higher conductivities than Si-I and *a*-Si,[5,8,9] it is thus advantageous to employ local probe techniques to image the distribution of the conductive phases. Conducting atomic force microscopy (CAFM),[10,11] which can simultaneously measure surface morphology and local current with a resolution of around 10 nm, is employed for a direct imaging of the distribution of the different structures. Local current-voltage (*I-V*) relationships have also been obtained to explore the electrical properties of the two conductive phases.

The indentation experiment was performed under ambient conditions using Berkovich diamond tips and two instruments: NanoIndenter XP (MTS, USA) and Triboscope (Hysitron, USA) (only for the 3 mN load). The samples were n-type (100) silicon wafers with a resistivity of 20 Ω cm. The loading and the unloading rates were both 1 mN/s, and the duration for the maximum load was 5 s. A commercial AFM (Smena-A, NT-MDT, Russia) and Au-coated tips[12] were used for the subsequent CAFM experiment. Positive voltage biases were applied to the tip with the substrate grounded. (Note that the application of negative biases would facilitate anodic nano-oxidation and obscure the measurement.[13]) Before each measurement, the indented sample was treated by diluted hydrofluoric acid (original 49% and dilution ratio 1:50) to remove the oxide layer. This step eliminated the complication of oxide thickness variation after indentation and produced a presumably homogeneous oxide layer.

At a maximum load of 50 mN, typical load-displacement curves with the discontinuity, the elbow, and both the effects are shown in Figs. 1(a)–1(c), respectively. The curves are similar to those in the literature.[2,3] The probabilities for the three occurrences at the maximum loads of 3, 5, 10, and 50 mN are listed in Table I. As can be seen clearly, the discontinuity effect is dominant at the load of 50 mN, but rare at other smaller loads. On the other hand, the elbow effect is dominant at loads other than 50 mN. The distribution is also in agreement with reported results.[2,3]

The topography and current images of an indented sample with the discontinuity effect after a maximum load of 50 mN are shown in Figs. 2(a) and 2(b), respectively. A tip bias of +1 V was used in the measurement. In Fig. 2(b), the

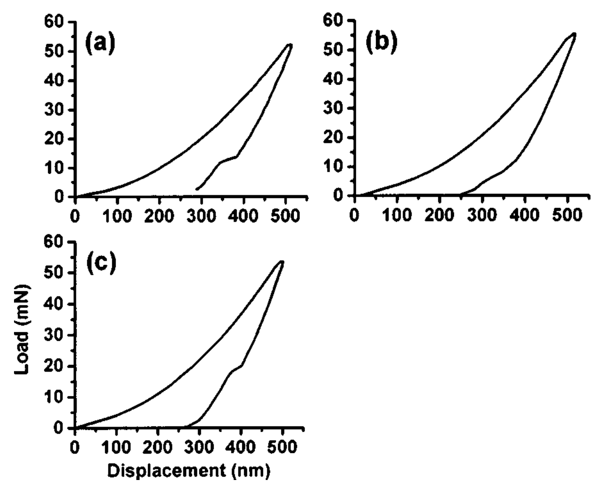

FIG. 1. Load-displacement curves showing (a) the discontinuity, (b) the elbow, and (c) both effects obtained with a maximum load of 50 mN.

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TABLE I. The probabilities for the occurrence of the discontinuity (D), the elbow (E), and both effects in the load-displacement curves at various loads.

Load (mN)	D (%)	E (%)	D and E (%)	# of tests
3	0	98.2	1.8	165
5	0.4	98.4	1.2	125
10	2.0	96.0	2.0	50
50	96.0	2.0	2.0	100

current on the flat region outside of the indent is at the noise level (~30 pA) and similar to that on the bright region in the indent. On the other hand, local currents on some locations in the indent are significantly higher. The high current sites can be conveniently defined as those having current values higher than 0.5 nA, which is roughly an order of magnitude higher than the noise current. Consequently, the high current sites can be directly related to Si-III and/or Si-XII, and the low current region to *a*-Si or untransformed Si-I. In addition, some of the high current sites have sizes down to 20 nm, suggesting the phase transformation occurs discretely on a nanometer scale.[4]

The results of more than a dozen samples with the discontinuity effect after the 50 mN maximum load all reveal the existence of high current sites. The distribution of high current sites varies from sample to sample, but the current values are in a close range. To exemplify such a consequence, the topography and current images of a different sample are shown in Figs. 2(c) and 2(d), respectively. On the two samples showing the elbow effect (see Table I), similar current images with the presence of high current sites are obtained. Although the elbow effect is strongly related to the formation of *a*-Si as mentioned previously, the present observation indicates that Si-III and/or Si-XII are generated concurrently (see below).

The results of two indented samples with the elbow effect after a maximum load of 10 mN are shown in Fig. 3, and the dramatic difference between the current images Figs. 3(b) and 3(d) is obvious. The former also has high current

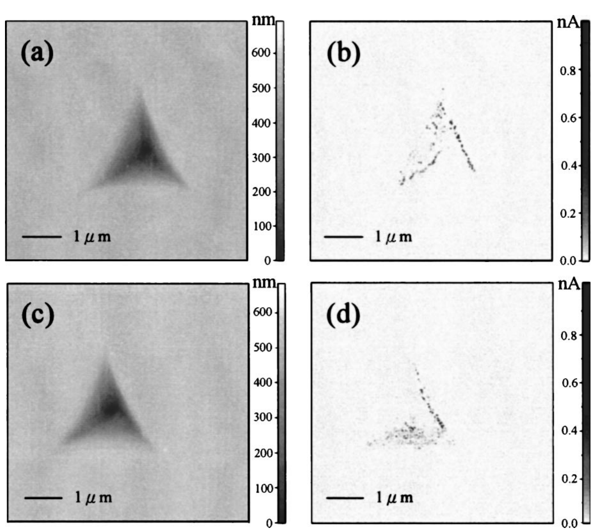

FIG. 2. (a), (c) topography and (b), (d) current images of two indented samples with the discontinuity effect after a maximum load of 50 mN. A tip bias of +1 V was used in both measurements.

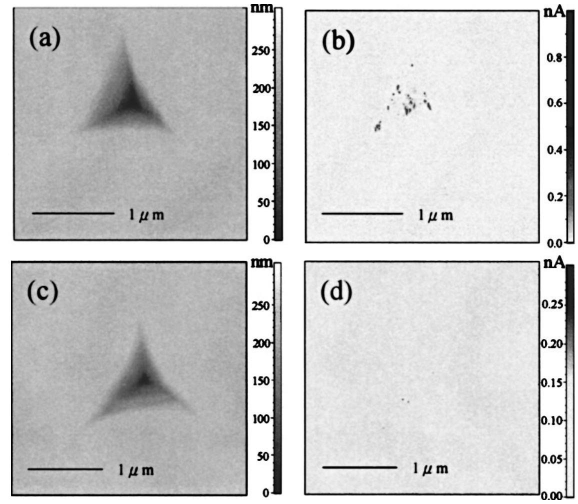

FIG. 3. (a), (c) topography and (b), (d) current images of two indented samples with the elbow effect after a maximum load of 10 mN. Different tip biases of +1 and +2.5 V were used to acquire (a) and (b), and (c) and (d), respectively.

sites with current values similar to those in Fig. 2. On the other hand, the latter has few high current sites with a largest value of only around 0.2 nA even with the application of a much higher bias of +2.5 V. The result clearly indicates the lack of Si-III and Si-XII in Fig. 3(d). It is apparent that an indentation associated with the elbow effect can produce Si-III and/or Si-XII, or none of them. Among the samples showing the elbow effect after the load of 10 or 5 mN, roughly 30% of them reveal no trace of high current sites. Consequently, our results are in disagreement with the assertion that the elbow effect is strongly related to the formation of *a*-Si reported by Gogotsi *et al.*[2] Nevertheless, a more detailed study by the same group has also identified both possibilities[3] and is consistent with our results.

To explore the electrical properties of Si-III and Si-XII, local *I-V* curves were also measured at the high current sites and a representative result is shown in Fig. 4(a). The relationship can be explained by the Fowler-Nordheim (F-N) tunneling in the Si-III (or Si-XII)/SiO_2/Au structure.[10,11,14] Both hole and electron tunneling can contribute to the measured current, but the former is negligible due to the larger energy barrier (~ 5 eV) between Au and SiO_2.[14] The measured current I due to electron tunneling from Si-III (or Si-XII) to SiO_2 at a large bias can be described by[10,11]

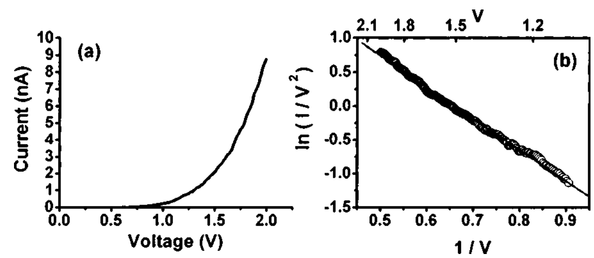

FIG. 4. (a) A representative *I-V* curve on high current site, and (b) the corresponding F-N plot at high voltage.

$$I = A\frac{e^3}{8\pi h\phi}\frac{m_0}{m}\left(\frac{V}{s}\right)^2\exp\left(-\frac{8\pi\sqrt{2m}}{3he}\frac{s}{V}\phi^{3/2}\right), \qquad (1)$$

where A is the tunneling area, e the electron charge, h the Planck's constant, ϕ the energy barrier, m_0 the free electron mass, m the effective electron mass in SiO_2, ($\sim 0.5m_0$), and s the oxide thickness. Note that the field enhancement due to the nonplanar tip shape and the image charge lowering of the barrier are ignored. The F-N plot is shown in Fig. 4(b) and clearly exhibits a linear relationship. Taking the oxide thickness as 2 nm,[15] ϕ is determined to be 0.61 eV from the slope in Fig. 4(b). More than 30 *I-V* curves have been measured on high current sites from indentations at various loads, and the values of ϕ are in the range of 0.6–1.1 eV and present no apparent dependence on the load. The fluctuation can be reasonably attributed to the variations in oxide thickness, tip-sample contact, size of high current site, etc. In addition, the barrier values are equally distributed, which prevents a differentiation between Si-III and Si-XII. Since it is difficult to accurately determine the parameters in Eq. (1), the obtained values of energy barrier can only be considered as estimates.[16]

To summarize, conducting atomic force microscopy has been employed successfully for imaging the phase transformation in Si nanoindentation. High current sites have been observed and correspond directly to Si-III and/or Si-XII. The observed smallest size is around 20 nm, suggesting that the phase transformation occurs on a nanometer scale. In addition, high current sites are always present in indentations showing the discontinuity effect, but observed only in part of the indentations showing the elbow effect. Local *I-V* curves on the high current sites exhibit electron tunneling behavior, and the energy barrier between Si-III (or Si-XII) and SiO_2 also has been estimated by fitting the results with the Fowler-Nordheim equation.

ACKNOWLEDGMENT

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[15] The nominal thickness of the natural oxide of Si is around 2 nm, which was also verified by transmission electron microscope measurement. Nevertheless, the oxide thickness of Si-III or Si-XII cannot be verified and the value of 2 nm is only for approximation.
[16] By assuming a tunneling area of 10 nm^2, the calculated current is in the range of μA from Eq. (1) and three orders of magnitude higher than the experimental values. It is also found that the calculated current value is in reasonable agreement with the measured values if a factor of 0.35, which represents the effects of the field enhancement and the image charge lowering, is multiplied into the exponential in Eq. (1). Using this value, the ϕ in Fig. 4(b) becomes 1.23 eV, which is twice as large as the previously obtained 0.61 eV.