Load Effects on Nanoindentation Behaviour and Microstructural Evolution of Single-Crystal Silicon

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Nanindentation tests are performed on single-crystal silicon wafers using a Berkovich indenter and maximum indentation loads of 30 mN, 40 mN, and 70 mN. The microstructural evolutions of the indented specimens are examined using transmission electron microscopy and selected area diffraction techniques. The results show that the unloading curve of the specimen indented to a maximum load of 30 mN has a smooth profile, whereas those of the specimens indented to 40 mN or 70 mN have a pop-out feature. The hardness and Young’s modulus of the silicon specimens reduce with an increasing indentation load, and have values of 15.8 GPa and 182 GPa, respectively, under the highest indentation load of 70 mN. In addition, a strong correlation is observed between the indentation load and the microstructural change in the indentation affected area of the silicon specimens. Specifically, a completely amorphous phase is induced within the indentation zone in the specimen indented to a maximum load of 30 mN, whereas a mixed structure comprising amorphous phase and nanocrystalline phase is found in the indentation zones in the specimens loaded to 40 mN and 70 mN. The microstructural observations imply that the load-dependent nature of the unloading curves is related to the occurrence of different phase transformation mechanisms under different indentation loads. [doi:10.2320/matertrans.M2010007]

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1. Introduction

Silicon has excellent semiconducting properties and is therefore widely used as a substrate material for many applications in the microelectronics and optoelectronics industries. The mechanical properties of the silicon substrate affect not only the mechanical performance of the device, but also its electrical and/or optical performance. Typically, silicon substrates are coated with a thin layer of silicon nitride or polyimide in order to protect the circuitry from the effects of the ambient environment, to relieve the stress induced during the flip-chip bonding process, to render the device more robust toward the effects of wear and tear, and so on.1–5) The presence of these thin films has a profound effect on the mechanical properties of the substrate, and thus many experimental studies have been performed to evaluate the properties of various thin films coated on a silicon substrate.4–8) However, the mechanical properties and nanoindented microstructures of silicon substrates under different loads are not yet fully clear. Therefore, further investigation is required into the effects of load on the nanoindentation response and microstructural evolution of silicon in order to establish the loading conditions which avoid the onset of plastic deformation and therefore improve the reliability of the device.

Nanoindentation provides a convenient means of analyzing the hardness and Young’s modulus of both bulk materials and thin films on a substrate.9) The loading and unloading regions of the load-displacement curves obtained in such tests commonly contain pop-in and pop-out events, respectively. It has been reported that the occurrence of these features is dependent on many factors, including the phase change induced within the indented microstructure, the indenter geometry and the loading-unloading rate.10–14) Silicon crystal is known to have a cubic diamond structure under normal atmospheric conditions.15) However, during nanoindentation, a pressure-induced phase transformation may occur within the indentation-affected zone.16) Since the mechanical response and phase transformation of a silicon substrate depend strongly on the magnitude of the applied load, a comprehensive study regarding the effects of load on the indentation behaviour and microstructural change is required. Accordingly, the present study utilises a nanoindentation technique to determine the loading-unloading characteristics of silicon substrates under different indentation loads in the range 30–70 mN. The microstructural evolutions of the indented specimens are then observed using transmission electron microscopy and selected area diffraction techniques. Finally, the observation results are used to clarify the load-dependent nature of the unloading curves obtained in the nanoindentation tests.

2. Experimental Procedure

The nanoindentation tests were performed using device grade p-type single-crystal silicon wafers with a (100) orientation. The wafers were 0.725 mm in thickness and were acquired with chemomechanical polished finishes. The nanoindentation tests were performed at room temperature in air using an MTS Nanoindenter XP system fitted with a Berkovich diamond pyramid tip with a radius of 20 nm. The specimens were indented to three different maximum loads, namely 30 mN, 40 mN and 70 mN. The loading-unloading procedure involved the following steps: (1) impressing the indenter until the pre-specified value of the maximum load was attained, (2) holding the indenter in this position for 1 s, and (3) smoothly withdrawing the indenter from the specimen over a period of 10 s. Five indentation tests were
performed under each experimental condition, and the corresponding hardness and Young’s modulus values of the silicon specimens were then calculated from the load-displacement curves using the Oliver and Pharr method. Following the nanoindentation tests, thin foil specimens for TEM inspection were prepared using an FEI Nova 200 focused ion beam (FIB) milling system with a Ga⁺ ion beam and an operating voltage of 30 kV. The cross-sectional microstructures of the various specimens were then observed using a Philips Tecnai F30 Field Emission Gun Transmission Microscope operated at 300 kV.

3. Results and Discussion

Figure 1 presents typical loading-unloading curves obtained when indenting the silicon specimens to maximum loads of 30 mN, 40 mN and 70 mN, respectively. It is observed that for each curve, the loading region has a smooth, continuous profile with no pop-in events. However, notably different features are observed in the unloading regions of the three curves. For example, for a maximum indentation load of 30 mN, the unloading curve contains a slight elbow (i.e. a gradual change in slope), which indicates a transformation from the original diamond cubic structure to an amorphous structure. By contrast, for maximum indentation loads of 40 mN and 70 mN, respectively, a well-defined pop-out feature is observed in the unloading region of each load-displacement curve. In other words, the critical load for the occurrence of pop-out is around 40 mN for the current silicon specimens. The pop-out features observed in nanoindentation tests have been attributed to many different factors. In the present single-crystal silicon specimens, the pop-out feature is thought to be the result of a phase transformation within the indentation-affected zone. Applying the Oliver and Pharr method to the experimental data presented in Fig. 1, it is found that both the hardness and the Young’s modulus decrease slightly as the maximum indentation load is increased from 30 mN to 70 mN (i.e. from 16.63 GPa to 15.70 GPa (hardness) and from 192.40 GPa to 182 GPa (Young’s modulus), see Table 1). The higher values of the hardness and Young’s modulus under a lower maximum indentation load can be attributed to the indentation size effect.

Figure 2 presents a bright field cross-sectional TEM micrograph of the silicon specimen indented to a maximum load of 30 mN. It can be seen that the indentation-affected zone (indicated by the dotted line) has a uniform microstructure and is separated from the surrounding area of the silicon specimen by a clear boundary. (Note that the long stripes in the region of the specimen outside of the nanoindentation-affected zone are simply interference fringes caused by a bending of the TEM sample during the FIB preparation process.) Figure 3(a) presents a high-magnification view of the morphology of the indentation-affected zone in Fig. 2. The inset in the lower right corner of Fig. 3(a) shows the TEM diffraction pattern of the indentation-affected zone. The presence of halo rings in this diffraction pattern indicates that the microstructure within the indented area is characterised by an amorphous phase. Figure 3(b) presents a high-magnification micrograph of the microstructure in the boundary region between the indented zone and the silicon substrate (corresponding to the square region indicated by label B in Fig. 2). The micrograph clearly shows that the indented zone has an amorphous structure, while the substrate has a crystalline structure.

Figure 4 presents a cross-sectional TEM micrograph of the silicon specimen indented to a maximum load of 40 mN. It can be seen that the indented microstructure changes from a fully amorphous state to a mixed amorphous/nanocrystalline state as the maximum indentation load is increased from

<table>
<thead>
<tr>
<th>Load</th>
<th>30 mN</th>
<th>40 mN</th>
<th>70 mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (GPa)</td>
<td>16.63</td>
<td>16.14</td>
<td>15.70</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>192.40</td>
<td>187.69</td>
<td>182</td>
</tr>
</tbody>
</table>

Fig. 2 Cross-sectional TEM micrograph of specimen indented to maximum load of 30 mN.
30 mN to 40 mN. This microstructural change is thought to be responsible for the pop-out event in the unloading region of the corresponding load-displacement curve shown in Fig. 1. Under a Berkovich indenter, the hydrostatic stress generated at the maximum indentation load initiates the formation of crystalline phase, while the octahedral shear stress breaks the bonds and leads to the formation of amorphous phase. Thus, in the present indentation experiments, the different maximum indentation loads result in different stress distributions under the Berkovich indenter, which in turn lead to different microstructural distributions of the amorphous and crystalline phase within the transformation zone. The phase transformation of the mixed microstructure beneath the indenter is accompanied by a sudden volume release, which leads to the pop-out phenomena observed in Fig. 1.

As discussed above, the microstructure of a transformed material is dependent on the maximum indentation load. Under a Berkovich indenter, the hydrostatic stress generated at the maximum indentation load initiates the formation of crystalline phase, while the octahedral shear stress breaks the bonds and leads to the formation of amorphous phase. This is thought to be responsible for the pop-out event in the unloading region of the corresponding load-displacement curve shown in Fig. 1. Under a Berkovich indenter, the hydrostatic stress generated at the maximum indentation load initiates the formation of crystalline phase, while the octahedral shear stress breaks the bonds and leads to the formation of amorphous phase. Thus, in the present indentation experiments, the different maximum indentation loads result in different stress distributions under the Berkovich indenter, which in turn lead to different microstructural distributions of the amorphous and crystalline phase within the transformation zone. The phase transformation of the mixed microstructure beneath the indenter is accompanied by a sudden volume release, which leads to the pop-out phenomena observed in Fig. 1.

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4. Conclusions

This study has evaluated the nano-mechanical properties of single-crystal silicon substrates indented to maximum loads of 30 mN, 40 mN and 70 mN, respectively. The effects of the load on the microstructural changes induced within the indented specimens have been characterised using transmission electron microscopy and selected area diffraction techniques. The results have shown that the loading curve has a smooth, continuous profile for all considered values of the maximum indentation load. However, for a maximum load of 40 mN or more, a well-defined pop-out feature is observed in the unloading region of the load-displacement curve. In addition, it has been shown that both the hardness and the Young’s modulus reduce slightly as the indentation load is increased. The observation results have shown that the phase indented to a maximum load of 70 mN (i.e. Fig. 6) is significantly higher than that in the specimen indented to a lower maximum load of 40 mN (i.e. Fig. 4).

Fig. 5 High-resolution TEM micrographs of regions indicated by: (a) square A in Fig. 4; (b) square B in Fig. 4.

Fig. 6 Cross-sectional TEM micrograph of specimen indented to maximum load of 70 mN.

Fig. 7 High-resolution TEM micrographs of regions indicated by: (a) square A in Fig. 6; (b) square B in Fig. 6.
transformation induced within the indentation-affected zone depends on the magnitude of the indentation load. Specifically, a small indentation load of 30 mN prompts the formation of a completely amorphous structure, whereas a higher load (i.e., >40 mN) gives rise to a mixed amorphous/nanocrystalline structure. Finally, it has been shown that the relative proportion of the nanocrystalline phase increases with an increasing indentation load.

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