Stress-Induced Amorphization of a Silicon Crystal by Mechanical Scratching

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(Received 31 March 1992)

The damaged layer induced in a silicon crystal by surface scratching at room temperature under a light load was found, by transmission electron microscopy, to be a small amorphous region surrounded by a dislocated crystalline region. No dent was detected on the surface and no crack was developed around the scratch. The amorphous region seems to be formed by phase transformation and not as the result of heavy plastic deformation of the crystal. The amorphous region was recrystallized to a dislocated crystalline region by annealing of the crystal at 600 °C.

PACS numbers: 64.70.Kb, 64.80.Gd, 81.40.Lm

When a dislocation-free Si crystal with a chemically polished surface is stressed at a high temperature, dislocations are observed to be generated heterogeneously in the surface region, under a stress which is lower than the theoretical shear strength by orders of magnitude, and to penetrate into the interior of the crystal [1]. This observation suggests that some fine flaws or structural irregularities exist even on chemically polished surfaces of a Si crystal and act as preferential generation centers of dislocations under applied stress.

The nature of surface defects in a Si crystal which were induced by scratching, indentation, or abrasion has been studied by many investigators. Since a very high stress is realized locally by scratching or indentation, some stress-induced phase transformations may take place there. Gridneva, Milman, and Trefilov [2] concluded that a crystalline region of Si transformed into the metallic phase as a result of indentation, from the observation of the change in the electrical resistance. Eremenko and Nikitenko reported that a hexagonal phase of Si was formed in the region around an indentation made on a Si crystal surface at high temperature [3]. A very high density of dislocations and microcracks has been observed in damaged layers induced by indentation, scratching, and abrasion [3–6].

Since these damaged layers have been investigated mainly by plan-view observations, the structure of the damaged layers is not well clarified.

In this Letter, we report the results of transmission electron microscopic observations of the structure of regions around scratches made on the (001) Si surface.

Specimens were cut from a dislocation-free Si crystal grown by the float-zone method which was n-type doped with P and had 1000 Ω cm resistivity. After chemical polishing, scratches were made on the chemically polished (001) surfaces of a specimen by a diamond stylus at room temperature. The scratches were drawn along the [110] direction with a load of 2 g at a scratching speed of 10 mm/s. Some specimens were annealed at 600 °C for 1 h in a vacuum after scratching, to observe the structural change in the damaged region.

Damaged regions that developed around scratches were observed both in plan view and cross sectionally by means of transmission electron microscopy (TEM). For plan-view observations the specimen was chemically thinned from the opposite side of the scratched surface. For cross-sectional observations two specimens were glued face to face and sliced perpendicularly to the scratch direction. Thin films for TEM observations were finished by mechanical thinning followed by Ar-ion milling. The specimens were observed with an electron microscope (JEOL 2000 EX) operating at 200 kV.

Figure 1 shows a plan-view TEM image of a scratch. Arrays of small half loops of dislocations are formed along the center and the periphery of the scratched region. Since the contrasts of these dislocations are found to disappear under the 040 diffraction condition, the Burgers vectors of the dislocation loops are thought to be either $(a/2)$ $[\bar{1}01]$ or $(a/2)$ [101], where a is the lattice parameter. A band of 0.7 μm in width and having light-dark contrast is seen at the central part of the scratch. This region has been examined by cross-sectional observations.

Figure 2(a) shows a cross-sectional micrograph of a scratch. A region with a round periphery about 1.4 μm

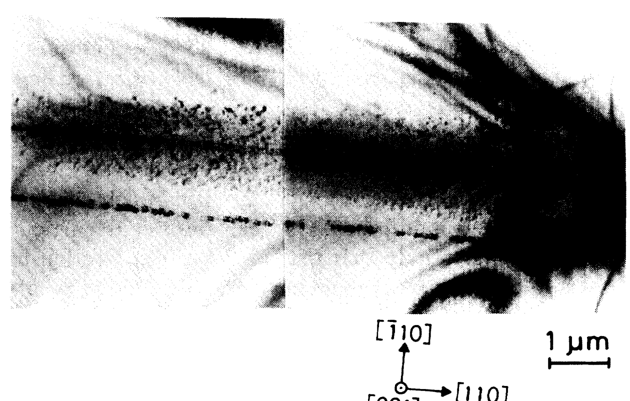

FIG. 1. Plan-view TEM micrograph of a region around a scratch on the (001) Si surface drawn along the [110] direction with a load of 2 g.

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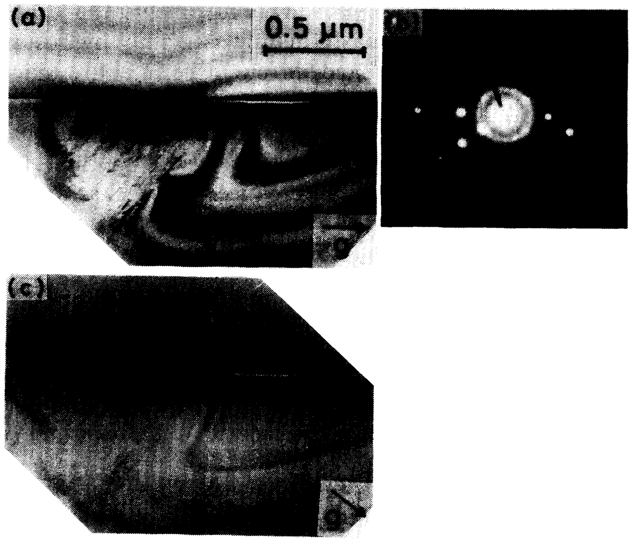

FIG. 2. Cross-sectional TEM micrographs of a region around a scratch taken with (a) $\mathbf{g}=\bar{2}20$ and (c) $\mathbf{g}=\bar{2}22$, where $\mathbf{g}$ is the diffraction vector. (b) Selected-area diffraction pattern from the scratched region.

in width and 0.15 μm in depth and having uniform dark contrast is seen to be developed in the surface region along the scratch. Figure 2(b) is the selected-area diffraction pattern from the area containing this region. It shows clearly two halo rings superposed on the diffraction spots from the (110) Si matrix crystal. Thus, we conclude that the dark region has amorphous structure. It is interesting to note that the surface at the scratch is flat and has no dent. Namely, scratching of the Si surface under a light load of 2 g does not produce a groove. Crystalline Si is seen to change to amorphous Si abruptly across the interface of the two regions. The interface is seen to be not very smooth, but rough. No polycrystalline layer or crack is seen to be developed around the interface. We conclude that the amorphous region has been formed by means of a phase transformation of crystalline Si under a localized high stress and not as the result of heavy plastic deformation.

Some dislocations lying on the planes parallel to the $(\bar{1}11)$ plane are observed to be introduced into the region just beneath the amorphous region. These dislocations show the minimum contrast under the $\bar{2}22$ diffraction condition as shown in Fig. 2(c), from which the Burgers vectors of these dislocations are known to lie on the $(\bar{1}11)$ plane. Since the Burgers vectors of dislocations are determined to be of the type $(a/2)\langle 110\rangle$ from the plan-view image in Fig. 1, these dislocations are thought to have been introduced by slip.

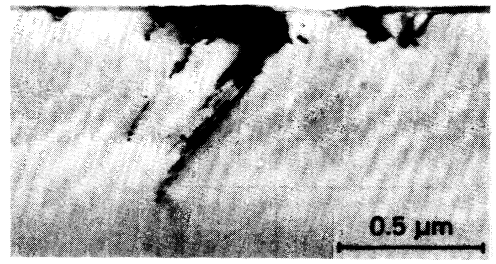

FIG. 3. Cross-sectional TEM micrograph of a scratched region annealed at 600 °C for 1 h.

Figure 3 is a cross-sectional micrograph of the scratched region after annealing at 600 °C for 1 h. Now, the amorphous region disappears and tangled dislocations are found along the scratch in the region up to 0.15 μm in depth from the surface. A hairpin dislocation is seen on the right side of the micrograph. Straight dislocations which lie in the region 0.15 to 0.8 μm in depth from the surface are those introduced by scratching. It has been reported that a Si amorphous layer formed on the surface of a Si crystal starts to crystallize at a temperature around 500 °C [7]. The amorphous region induced by scratching in our case is thought to have recrystallized by annealing into a crystalline region containing tangled dislocations and hairpin dislocations.

We estimate the magnitude of stress realized in the region beneath the scratch. For simplicity, we assume that a diamond stylus is in elastic contact [8] with a Si surface and that the scratching process is quasistatic; namely, the load is distributed uniformly over the contact circle of radius R. Taking the cylindrical coordinates as shown in Fig. 4, stresses σ_z, σ_r, and σ_θ are given as follows:

$$\sigma_z=(P/\pi R^2)[z^2/(R^2+z^2)-1]\,, \tag{1}$$

$$\sigma_r=\sigma_\theta=(P/2\pi R^2)[-(1+2\nu)+2(1+\nu)z/(R^2+z^2)^{1/2}-z^3/(R^2+z^2)^{3/2}]\,, \tag{2}$$

where P is the load and ν is Poisson's ratio for the Si crystal. The maximum shear stress τ is given by

$$\tau=(\sigma_r-\sigma_z)/2=(P/4\pi R^2)[(1-2\nu)+2(1+\nu)z/(R^2+z^2)^{1/2}-3z^3/(R^2+z^2)^{3/2}]\,. \tag{3}$$

τ takes its maximum value at the depth

$$z=R[2(1+\nu)/(7-\nu)]^{1/2}\,.$$

With $\nu=0.215$ [9], $P=2$ g, and $R=0.7$ μm from Fig. 2(a), the maximum value of τ turns out to be 4.49×10^3 MPa, which is close to the theoretical shear strength of a perfect Si crystal calculated to be 1.39×10^4 MPa [10]. Thus, it is

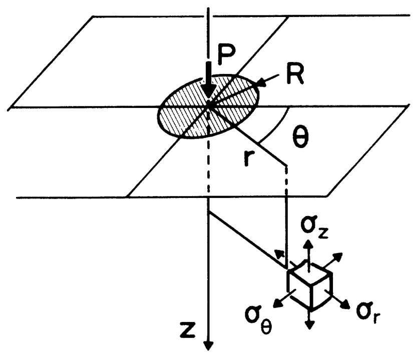

FIG. 4. Geometry of quasistatic scratching.

probable that slip dislocations are generated in the region beneath the diamond stylus used to make the scratch.

High-pressure experiments with a diamond anvil [11] have revealed the phase changes of a Si crystal as follows: Crystalline Si with the diamond structure transforms to the simple hexagonal structure phase at 100 K under high pressure up to 13 GPa. On reducing the pressure, the simple hexagonal phase transforms to the β-Sn structure phase, and the latter structure is frozen for pressures down to 2 GPa. When the crystal in such a β-Sn phase is heated to a temperature of 300 K, keeping the pressure at 2 GPa, it transforms to the amorphous phase. Under high pressure at room temperature a Si crystal with the diamond structure never transforms to the amorphous phase but to the simple hexagonal structure phase via the β-Sn structure phase when the pressure is raised to 15 GPa. Si in such a high-pressure phase does not transform to the amorphous phase even when the pressure is removed. In these high-pressure experiments the driving force for the phase transformation is mainly hydrostatic stress. On the other hand, in our experiment, a silicon crystal with diamond structure amorphized as a result of scratching at room temperature and the amorphous phase was frozen even if the load was removed. We think that the very high shear stress produced by the scratching causes the amorphization of the silicon crystal with diamond structure as a result of a phase transformation.

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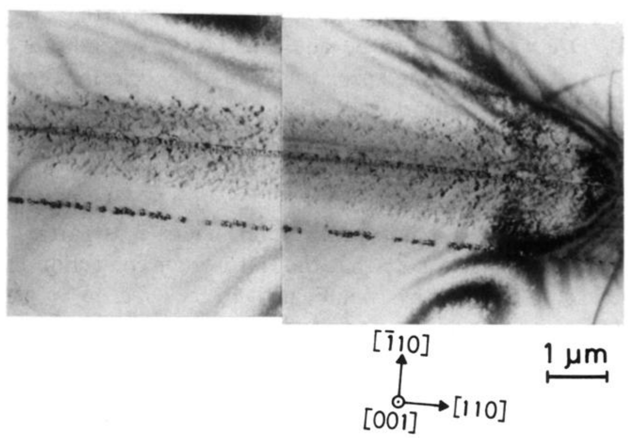

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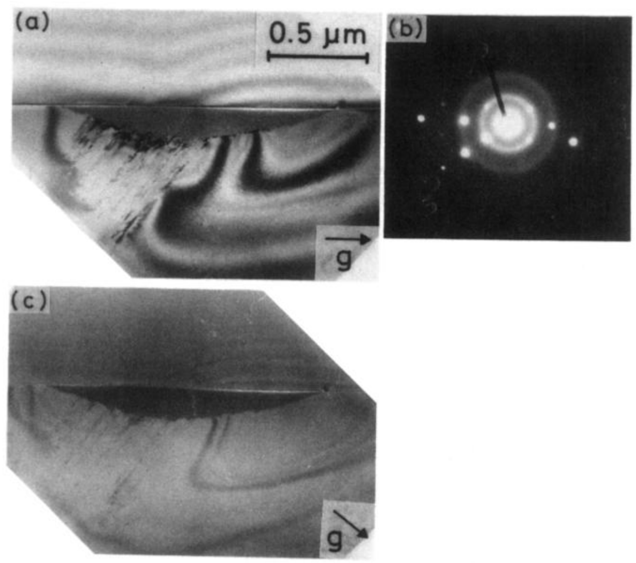

FIG. 2. Cross-sectional TEM micrographs of a region around a scratch taken with (a) $\mathbf{g}=\bar{2}20$ and (c) $\mathbf{g}=\bar{2}22$, where **g** is the diffraction vector. (b) Selected-area diffraction pattern from the scratched region.

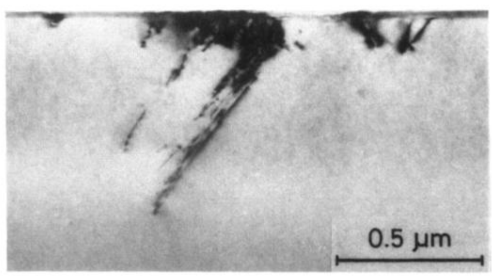

FIG. 3. Cross-sectional TEM micrograph of a scratched region annealed at 600 °C for 1 h.