Experimental study of dislocations in single crystals of the fullerene C_{60} and mechanisms for plastic deformation of these crystals

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Selective-etching methods have been developed for visualizing dislocations and other defects in C_{60} single crystals. The nature of the changes which occur in the actual crystal structure as the result of plastic deformation during microindentation of the surface was studied. The crystallography is analyzed. Aspects of dislocation glide and crack formation in C_{60} crystals are analyzed. Effects which result from holding the samples in air at various temperatures and in a solvent are described. Effects of illumination of the crystal with visible light are also described.

The ability to synthesize solids based on a fullerene—a new form of carbon, consisting of closed spherical molecules at the sites of a crystal lattice[1,2]—has opened the door to the development of new materials with special physical properties. In particular, these materials constitute new classes of high-T_c superconductors and organic ferromagnets. These materials have some extremely interesting optical, electrical, and chemical properties.

There has been essentially no experimental study of the dislocation structure of fullerene crystals or of the mechanisms for plastic deformation of these crystals. Only a few studies have been carried out. In these studies attempts have been made to analyze macroscopic characteristics of the plastic deformation of C_{60} and C_{70} crystals.[3–5]

In this letter we are reporting preliminary results of research aimed at developing a method for selective etching for visualizing dislocations and other lattice defects in C_{60} crystals. Selective etching is the simplest and fastest of the vast arsenal of methods available for monitoring structural defects. It furthermore does not destroy the sample. The method which has been developed has been used to study the changes which occur in the actual structure of single crystals of the fcc fullerene C_{60} subjected to a concentrated load. The purpose of this study was to identify the basic physical mechanisms responsible for the microplastic deformation of this material.

The C_{60} single crystals were grown from the vapor phase by the method described in Refs. 6 and 7. The starting material was a fine-grain C_{60} powder prepared by the procedure of Ref. 8, involving graphite chromatography. The purity of the powder was monitored by mass spectroscopy. The C_{60} concentration in the powder was more than 99.9%. The starting powder was placed in a quartz cell, which was evacuated to 10^{-5} torr and heated to 250 °C. As the powder was held in a dynamic vacuum for several hours, organic solvents were removed from it. The powder was then subjected to vacuum sublimation three times.

The purified powder was put back in the cell, which was then evacuated to 10^{-6} torr and sealed off. The growth was carried out at a sublimation temperature of 500 °C, at a crystallization temperature of 480 °C, and with a crystal growth time of 8 h. The products were faceted C_{60} single crystals with volumes up to 3 mm^3.

The crystals were deformed by microindentation, which was carried out with the help of a special attachment to a Neophot-2 optical microscope at room temperature. The indenter was a Vickers diamond pyramid. As the indenter is pushed into the crystal surface, a complex stress field arises. In addition to substantial tangential stresses, there is a hydrostatic component in the region below the indenter. This circumstance (along with the fairly rapid decrease in the stress with distance from the point at which the load is applied) has the consequence that, even in the case of extremely brittle materials, the cracks of critical size which are generated do not propagate over the entire sample and do not lead to a catastrophic fracture of the sample. Under these conditions it is possible to observe manifestations of all possible plastic-deformation mechanisms (dislocation glide, the formation and motion of point defects, twinning, and phase transitions) and to study the crystallographic characteristics of these mechanisms.[9,10]

The study showed that selective etching to visualize dislocations and other lattice defects in C_{60} single crystals can be carried out by thermal and chemical etching of the surface of the sample. Fairly high-contrast etching pits can be produced by exposing the

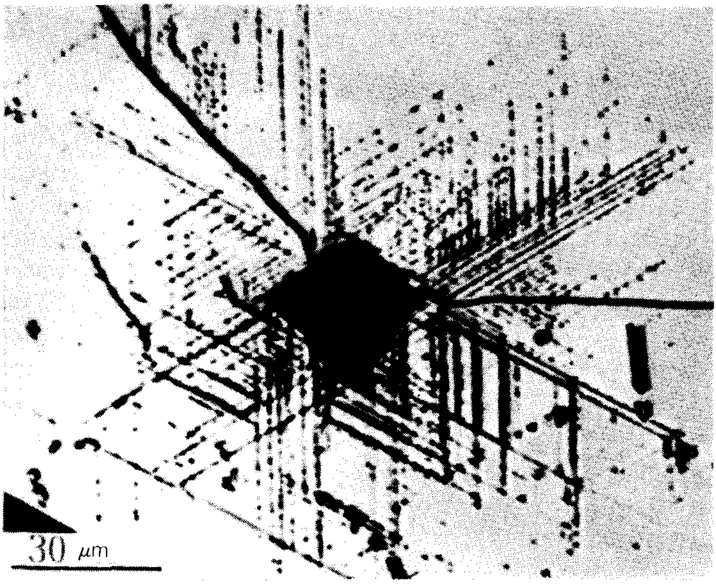

FIG. 1. Dislocation rosette around the imprint left by the indenter on a {111} surface of a freshly grown single crystal of the fullerene C_{60}. This rosette became visible after selective chemical etching in toluene (the load on the indenter was 10 g; room temperature).

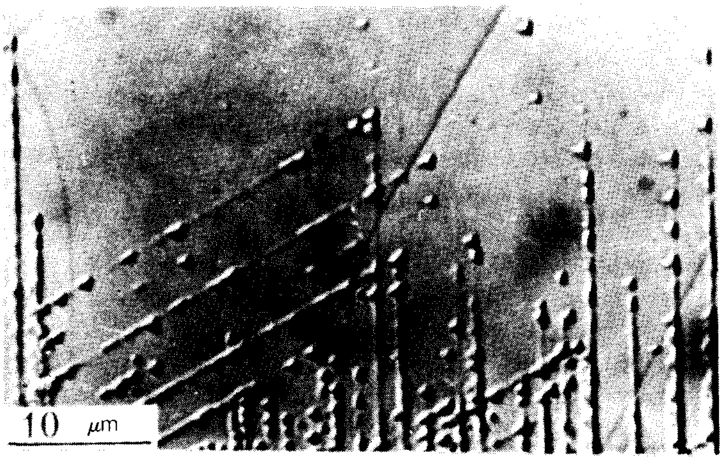

FIG. 2. Dislocation etching pits and glide tracks which were etched behind moving dislocations.

crystals to air at 450 °C for 30–40 min. A selective chemical etching is achieved by immersing the sample in toluene for 10–15 s.

Pushing the indenter into the surface of crystals which had been stored in air for no more than a few hours resulted in the formation of an imprint, around which only glide lines were observed at loads up to 20 g. The symmetry of the arrangement of these lines on the {111} and {100} surfaces indicates that they form because of displacement along {111} planes. When a cell with the as-grown crystals is opened up, and the samples are exposed to air for a short time, the indentation of the surface does not lead to the formation of cracks visible under a microscope.

After chemical etching, we observed not only a dislocation rosette (Fig. 1), but also several radial cracks, which started at the imprint left by the indenter, along the glide lines. At high magnification (Fig. 2) we see that both etching pits on isolated dislocations and continuous grooves of a lower contrast are etched along a glide plane. These grooves may arise because of point defects which form and undergo a redistribution in the course of the motion of dislocations. Similar marks have been etched on silicon single crystals behind gliding dislocations.[11] We found no indication that other mechanisms (twinning and phase transitions) are involved in the plastic deformation of this fullerite.

In the left-hand corner in Fig. 1 there is a line which visualizes a defect which formed during the growth of the crystal and which acts as a barrier to the glide of dislocations away from the indenter imprint. The nature of the etching of this defect is similar to that which has been observed in the case of semiconductor single crystals with stacking faults or thin twin interlayers. The cracks visible in Fig. 1 probably formed during the indentation, but they were not observed in a metallographic inspection. At the points where a crack has stopped, there is a relaxation of the stress due to the formation and motion of dislocations, as can be seen from the nature of the arrangement of the glide tracks along the cracks.

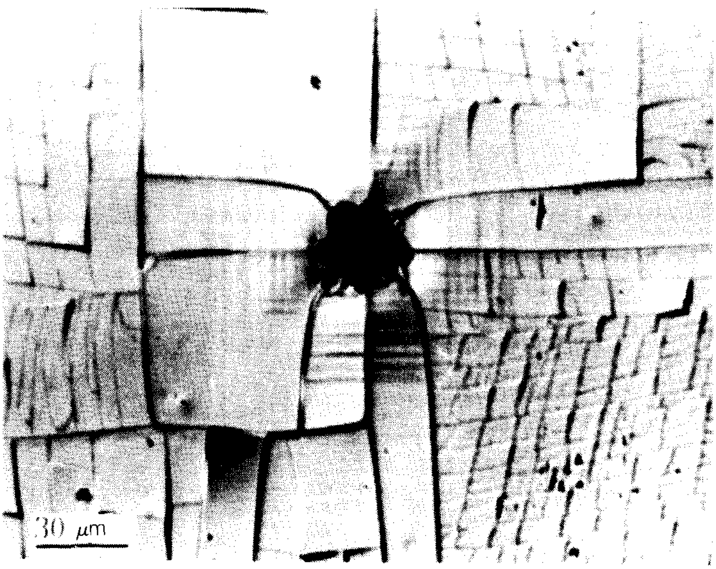

FIG. 3. Imprint left by the indenter in a {100} face of a single crystal of the fullerene C_{60} which was stored in air at room temperature for a long time, after a 15-min annealing at 450 °C and illumination with visible light for 1 h (indenter load of 5 g; room temperature).

Exposing the crystal to air reduces the plasticity of the surface layers of the crystal. When the sample is stored in air for a long time, the surface becomes so brittle that the application of the indenter results in the observation of only a system of radial and tangential cracks; no traces of plastic deformation by glide are observed. The cracks are directed predominantly along $\langle 110 \rangle$ directions. Despite the rather severe cracking, the crystal retains its integrity. This result means that the cracks penetrate only a thin surface layer and do not propagate into the interior of the sample.

Annealing a crystal at 450 °C for 15 min in air results in the formation of glide lines along the imprint. These lines run parallel to $\langle 110 \rangle$ directions (Fig. 3). When a sample is inspected under an optical microscope, and illuminated with visible light for about 1 h, the crystal suffers further cracking.

These results indicate that only freshly grown single crystals have a high plasticity. When the crystals are stored in air and illuminated with visible light, the surface layers of the crystals age rapidly, probably because of an oxidation.

In summary, these results show that the primary mechanism for the plastic deformation of crystals of the fullerene C_{60} is glide due to the formation and motion of dislocations. It is highly likely that, as for all fcc crystals, the glide planes for these dislocations are $\{111\}$ planes, and the Burgers vector is along a $\langle 110 \rangle$ direction. These experiments have also revealed that exposing the samples to air or illuminating them with visible light makes the samples more brittle.

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