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Growth and mechanical property of C_{60} single crystals

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C_{60} single crystals were grown from vapor by repeated growth method using the resulting small crystals as the source materials. Consequently single crystals up to a size of $0.5\times1.0\times1.5$ mm^3 were obtained. The mechanical property, i.e. Vickers hardness, of the growth crystal was investigated using microhardness indentation technique. The temperature dependence of the hardness was measured at temperatures between room temperature and 240 K. The experimental results showed that the hardness tend to increase with the decrease of temperature. However, a discontinuous change in the hardness was observed at around 255 K. Such sharp change can be related to the phase transition of C_{60} crystal.

1. INTRODUCTION

The interesting physical and chemical properties of C_{60} materials including superconductivity of alkali metal doped C_{60} materials and interesting phase transitions have stimulated a dramatic spread of research activities. To date, most of the works were done on polycrystalline samples or on thin films. However, a detailed understanding of the properties of the C_{60} materials can only be achieved from a study of single crystals of these materials. In particular, the study of mechanical property such as the hardness need a number of high quality single crystals of sufficient size for the measurment. So papers which studied the mechanical property using the single crystal has been limited in numbers [1,2].

C_{60} single crystals may be prepared from solution of pure C_{60} in suitable solvents (benzene, *n*-hexane, CS_2, pentane etc.)[3,4]. However, the solution-grown crystals have been known to include a significant amount of the solvent molecules and to exhibit different structures depending on the solvent used. The problem of solvent inclusion can be eliminated by sublimation growth. In the case, highly pure single crystals can be grown [5]. Various growth techniques based on the sublimation method have been developed. Their growth is carried out in vacuum [1,5,6] or in an inert gas atmosphere [7] using a periodic oscillation of crystal temperature [1] or a double-temperature gradient [6].

In this work, C_{60} single crystals were grown by improved vacuum sublimation method with temperature gradient, in which the resulting small crystals are used repeatedly as the source materials. Consequently C_{60} crystals of millimeter size were obtained. Employing these crystals, mechanical property, i.e. Vickers hardness, were investigated. The dependence of the hardness on the temperature were measured.

2. EXPERIMENTAL

2.1. Crystal growth

The starting purified C_{60} powder was deposited onto the closed end of 7 mm inner diameter long pyrex tube. The tube was evacuated to 1×10^{-5} Torr. Then the tube was sealed off so that its length was about 15 cm. The source material was at one end of the tube and the other was empty. The tube was placed in a horizontal furnace with two temperature zones. The temperatures at the two ends of the tube could be controlled independently. The source temperature was kept at 620 °C. The temperature at the other end of the tube was kept at 460 °C. To grow the crystal, these conditions were maintained for about 24 hours. After the crystal growth the temperatures of both regions were decreased down to room tempera-

ture in about one hour. The resulting small crystals were used as the source materials for next crystal growth. This process was repeated more than two times. The habit faces of the larger crystals obtained finally were confirmed by the transmission Laue method. The morphologies of the crystals were observed by the optical microscope. Furthermore X-ray topographic observation was made for these crystals to examine the crystal perfections.

2.2. Hardness measurements

Hardness measurements were carried out by using a Akashi Microhardness Tester with a diamond pyramidal indenter. The apparatus was modified for the measurement of temperature dependence of Vickers hardness. The value of the Vickers hardness Hv was measured on the (111) habit face of C_{60} single crystal. Thus crystals with well-developed (111) face were selected for the hardness measurement. The specimens were fixed on copper substrate by silver paste to keep the (111) crystal face perpendicular to the diamond indenter. The indenter was pulled down to the specimen surface with velocity of 0.01 mm sec^{-1}. Contact period of the indenter with specimen surface was chosen to be 5 seconds.

First the Vickers hardness was measured as a function of load at room temperature. Next the temperature dependence of the Vickers hardness was investigated in a temperature range of room temperature and 240 K. Then 3 g weight load was selected. The hardness was measured in about 5 K steps at a cooling rate of 0.3 K min^{-1} in nitrogen gas atmosphere. Temperature was measured by an alumel-chromel thermocouple inserted in the copper holder.

3. RESULTS AND DISCUSSION

3.1. Growth crystals

Single crystals up to a size of $0.5 \times 1.0 \times 1.5$ mm^3 were obtained. Figure 1 shows the typical growth crystals taken by optical microscope. The crystals had a polyhedral shape with smooth and shiny habit faces such as {111} and {100} of the face centered cubic (fcc) structure, which is room temperature structure of C_{60} crystal. The orientation of the well-developed (111) face was assigned by the Laue method.

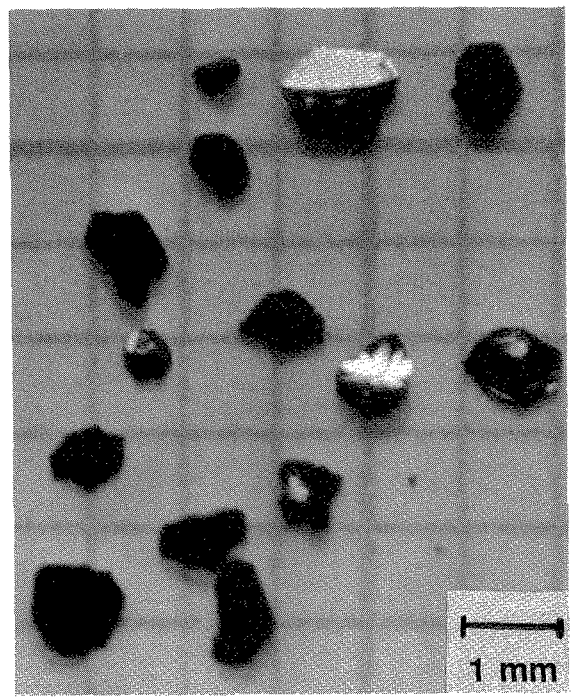

Figure 1. Typical C_{60} crystals grown from vapor.

The optical microscopic observations also showed that, in some cases, interesting morphologies, such as dendrites and systematic cracks, were developed at the surfaces of the crystal. Similar phenomenona had been observed also on C_{60} crystals obtained by Haluska et al [6]. The origin of such morphologies is not known yet.

X-ray topograph of the C_{60} crystal could be obtained using Lang method and using synchrotron radiation method. However the well-resolved crystal defects could not be observed yet. This may be because the crystal is too small or the structural perfection of the crystal is poor although the quality of the crystal surface seem to be good from the optical microscopy. For X-ray topographic studies, crystals of a size at least more than 3-5 mm are thought to be required.

3.2. Studies of microhardness indentations

The indentations were made only on relatively good quality part in well-developed (111) face, judged from the optical microscopic observation, since the Vickers hardness is sensitive to the surface morphology of the crystal.

At room temperature, the hardness measurements were carried out as a function of load. The hardness remained constant with load, except for that more than load of 25 g which lead to deformed impressions of indentations on the habit face. The value of the Vickers hardness of C_{60} crystals for the (111) face was about 23 at room temperature. Within experimental error, this value was in satisfactory agreement with the value measured by Li et al. [1]. Thus it seems that C_{60} crystal is a soft material, which is almost the same as that of pure gold.

The hardness measurements were also carried out as a function of temperature. Taking into account for shapes of indentations formed using various loads at room temperature, 3 g was selected as an applied load. Figure 2 shows the temperature dependence of the Vickers hardness.

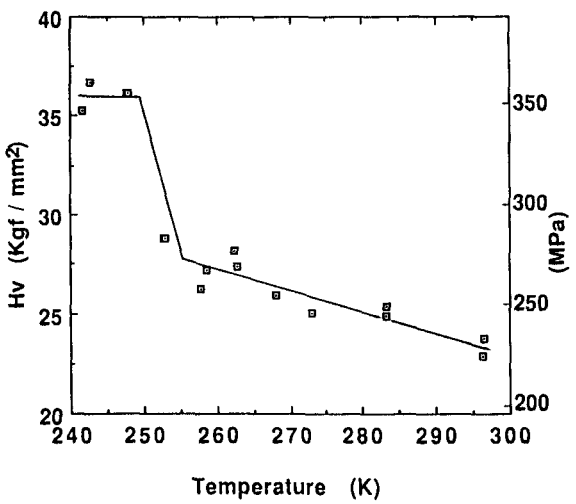

Figure 2. Temperature dependence of Vickers hardness Hv of C_{60} single crystal.

In the temperature range from room temperature to 240 K, the hardness increases with decreasing temperature. The temperature dependence of the hardness is quite strong, compared with another organic crystals. It is noteworthy that the hardness drastically increases at around 255 K. This temperature corresponds to that of the phase transition of C_{60} crystal from the fcc to simple cubic (sc) structure. Thus the drastic increment of the hardness can be related to the phase transition. The phase transition at 250 $\sim$ 260 K have been revealed by many experiments, e.g. XRD [1,8], NMR [9], sound velocity [10], electrical conductivity [11], electrical resistivity [12], thermal conductivity [13]. Thus the present experimental results also indicate that the phase transition can be confirmed by the hardness measurement.

One of origins of the hardness is due to the plastic deformation around the indentation, which can be occurred by the generation of dislocations. Thus the hardness is related to the formation energy of dislocation. The energy mainly depend on the magnitude of Burgers vectors of dislocations. According to energetic criterion, the shorter lattice translational vectors are favoured as Burgers vectors in crystals [14]. Thus, in the C_{60} crystal with fcc structure, the production of 1/2[110] (10.0 $\AA$) Burgers vector has highest probability. On the other hand, in the sc crystal, the possible Burgers vector is [100] (14.0 $\AA$), which is longer than that in the fcc crystal. Therefore the dislocation elastic energy in the sc crystal become high compared with that in the fcc crystal. This means that it is difficult to generate dislocations in the sc crystals. This may be reason why the Vickers hardness abruptly increases in the phase transition from fcc to sc structure.

Systematic crack lines were observed on the (111) face after indentation, as shown in fig. 3. The length of the crack line was strongly correlated with the value of the hardness. That is to say, the higher the hardness is, the longer the length of crack line become. The detailed analysis of various crack lines induced by the indentation is in progress.

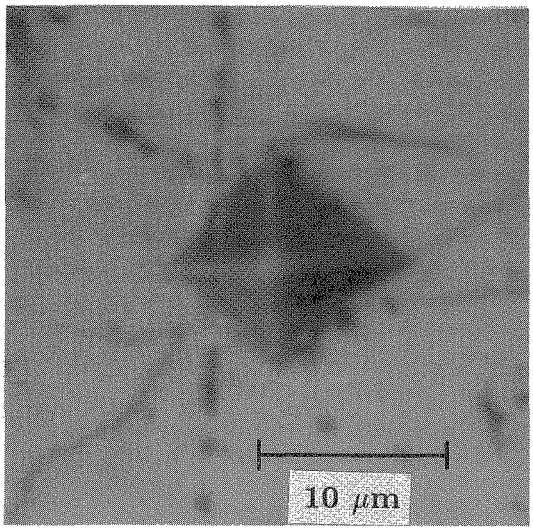

Figure 3. Diamond pyramid indentation formed at 3 g load on the (111) habit face of C_{60} single crystal. Crack lines are observed.

4. CONCLUSIONS

C_{60} single crystals were grown from vapor up to a size $0.5 \times 1.0 \times 1.5$ mm^3 by repeated growth method using the resulting small crystals as source materials. The value of the Vickers hardness at room temperature showed that the C_{60} crystal is soft material. Furthermore, the measurement of the Vickers hardness from room temperature to 240 K revealed a phase transition from fcc to sc at around 255 K.

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