

Growth and Electric Properties of C₆₀ Nano-Crystals Directly Grown between Electrodes from Solution by Dipping Technique

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1. Introduction

Since the C₆₀ nano-whisker (C₆₀-NW) is simply able to be grown by the liquid liquid interfacial precipitation (LLIP) method, the electric properties, leading to the field effect transistor (FET), of C₆₀-NW have been paid attention again in the same way to that of carbon nanotube due to its particular needle-like shape.[1] The highest mobility of C₆₀ thin films as a n-type semiconductor is 1.4 cm²/Vs without exposure to the air, as far as authors know.[2] The solution including the C₆₀-NW is dropped between source-drain electrodes, and then after it dries the FET properties of C₆₀-NW is demonstrated.[3] Although the electric property of C₆₀ crystal is rapidly degraded in air, it seems that the C₆₀-NW grown from solution has less reactivity in the air. It is probably due to the polymerization and/or intercalation of the solvent molecules in the as-grown C₆₀-NW.[4] Furthermore the nano-scale C₆₀-NW is reported to be conductive.[5]

In order to realize the FET device with good performance with C₆₀-NW in a nano-scale, both of the top-down technique and bottom-up technique must be combined. The electrodes were deposited through a metal mask, or were prepared by a traditional lithography. The C₆₀-NW was self-assembly grown between electrodes from solution by dipping method. The C₆₀-NW was not grown by the LLIP method but just by evaporation of solvent from saturation solution dissolving C₆₀ molecules. We have already reported the C₆₀ crystal growth from solution by just evaporating solvent.[6] Indeed the crystal structure, crystallinity, shape, and growth direction *etc.* are expected to depend on solvent, dipping speed, and solution temperature, electrode's shape, difference in surface tension between solvent and the substrate surface (wettability), and so forth. In this report crystal growth and electric properties of C₆₀ crystal self-assembly grown between electrodes were investigated.

2. Experimental

The electrodes were deposited by an evaporation method through a metal mask on 300nm-SiO₂/Si substrates. The electrode is consisted of two parts. One of them is a pad with the size of 300 μm×300 μm to connect electrically to the measurement system of resistance. The other one is so-called source and/or drain rectangular electrodes with the size of 50 μm × 100~135 μm. The gap between the rectangular electrodes is from 100 μm to 30 μm. The solution that dissolved C₆₀ used the toluene. The electrodes deposited substrates were soaked in the saturation solution dissolving C₆₀ molecules for *T_s* of 0 min

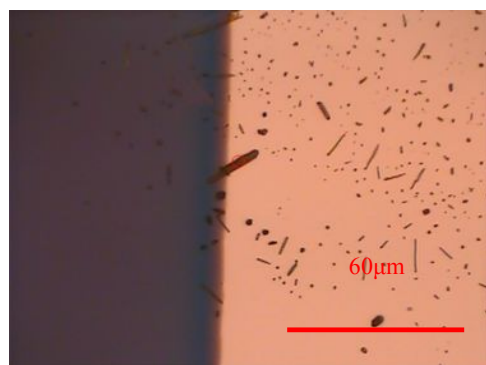
and 10 min. The substrates were drawn up with the speed, *V_D*, of 1 μm/sec and 100 μm/sec. The all dipping procedures were carried out at room temperature. The grown C₆₀ crystal shape was examined by an optical microscope. The X-ray diffraction was done at the 100 μm-area (Rigaku International Corp.: RAD-C). The micro-Raman spectra were obtained with the area of 2 μm with the 532 nm excitation laser, which is second harmonic of YAG laser (Kaiser Corp.: Holo Lab 5000R). During the micro-Raman spectra measurement the optical image was also observed with a 50 magnification times microscope.

3. Results & Discussion

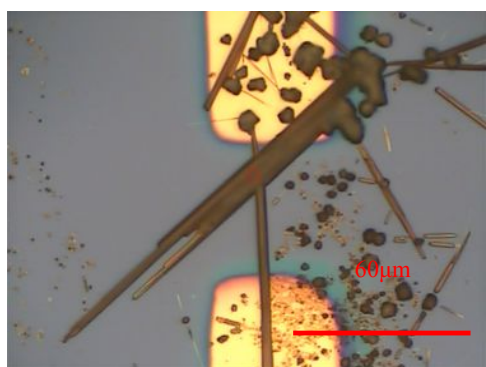
Figure 1(a) shows a typical optical microscope image around electrode pad: right half is an electrode, left half is substrate surface. The substrate was soaked into the saturation solution, and then immediately was drawn up with *V_D* of 1 μm/s, indicating that the *T_s* was zero. A lot of Particles and whiskers were found on Au electrode pad not on substrate. Any particles and/or whiskers were not found between the source/drain electrodes gap. The maximum length of whiskers was approximately 20 μm. Figures 1(b) and 1(c) show the images around the gap between rectangular source and/or drain electrodes with *T_s* of 10 min and *V_D* of 1 and 100 μm/s, respectively. On the contrary to the result mentioned above in Fig.1(a), particles and whiskers grew between the gap on the source/drain electrodes. The longest whisker with 120 μm was seen in Fig.1(b). In Fig.1(c), particles and whiskers grew on and around the electrodes, however whiskers did not bridge the source/drain electrodes. It was rare to find any particles and whiskers on the substrate surface.

The reason why the growth of particles and whiskers between on electrodes and on substrate surface is so different is expected to be the wettability. The hydrophobic solvent, toluene, is more adhesive to Au surfaces rather than to hydrophilic SiO₂ surfaces. The growth direction of whiskers was random as shown in Fig.1(b) and 1(c). The C₆₀ molecules precipitated by evaporating the remained solvent from the substrate surface just after the substrate was taken out of the saturation solution. There seems to be no reason to decide the growth direction. Therefore some guide is necessary to determine the growth direction. Increasing the *T_s*, the amount of particles and whiskers was also increased comparing Fig.1(a) and Fig.1(b), 1(c). During maintaining the substrate in the solution, the solvent evaporates, and some C₆₀ molecules precipitate on the surface probably to be a nucleation cites. At faster

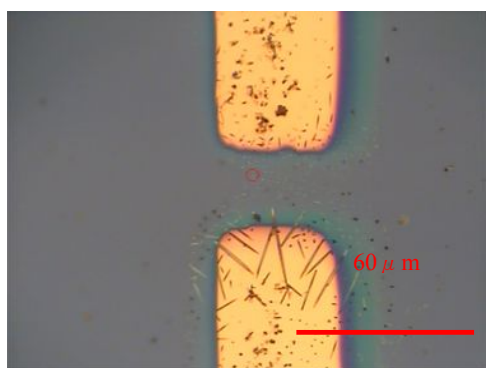
dipping speed as shown in Fig.1(c), smaller grains and whiskers grew. It is reasonable to expect that the volume of the remained solution per unit area, where the C_{60} molecules start to precipitate, is smaller, and then only smaller particles/whisker grew.



(a) $t_s=0$ min, $v_d=1$ $\mu\text{m/s}$



(b) $t_s=10$ min, $v_d=1$ $\mu\text{m/s}$



(c) $t_s=10$ min, $v_d=100$ $\mu\text{m/s}$

Fig.1 Optical microscope image of typical precipitated C_{60} crystals.

Figure 2 shows the result of the X-ray diffraction of particles and whiskers shown in Figure 1. The Bragg peaks of (111), (220), and (311) of fcc C_{60} crystals were found. Comparing to the bulk value, the lattice spacing was bigger with approximately 3 %. It is caused by the polymerization of C_{60} molecules.

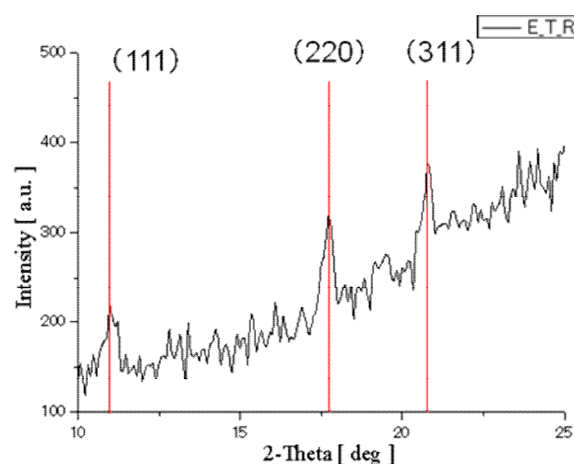


Fig.2 The reflected X-ray diffraction of FFW

The Raman spectrum of the precipitated film showed peaks of Ag(2) mode at 1469cm^{-1} and lower side of the Ag(2). The shift to lower energy side of Ag(2) mode indicates the polymerization, which is consistent with the indication of the XRD results.

4. Conclusions

The size of C_{60} -NW could be controlled by changing the dipping condition. The long soaked time helped the formation of the crystalline nucleus. The growth direction in whiskers needs guiding for the control. We thought that the difference of the growth of C_{60} -NW on the electrode and the substrate was caused from the each hydrophobic or hydrophilic property.

References

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