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SYNTHESIS OF AxC60 FILM BY ELECTROLYSIS

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Abstract The electrolysis was adopted to obtain the AxC60 (A=Rb) film from an organic electrolyte solution including C60 molecules. The used solution was a mixture of 0.3mM-C60, 0.1N-RbClO4 and dimetyleformuamide (DMF) / Toluene (1:1). The particles in the obtained film had a spindle-like shape and grew up to the size of about 1 μ m depending on the reaction temperature. The Raman spectra of the obtained films showed the existence of solid C60 and revealed the features of the polymeric Rb1C60, of which the crystal structure was confirmed a body-centered-orthorhombic phase by X-ray diffraction.

INTRODUCTION

The discovery of fullerenes[1] has brought us a new class of carbon-based solids as functional materials. An alkali-metal (A) -intercalated C60,AxC60 has been widely studied because of its interesting properties, for example superconductivity[2,3]. Several crystal phases of the AxC60 have been found: a face-centered cubic (fcc) A1C60, an fcc A3C60, a body-centered tetragonal (bct) A4C60, and a body-centered cubic (bcc) A6C60.[4-6] A polymeric C60 compound as a new characteristic phase has also been mentioned. Then C60 molecules are linked with each other by covalent bonds formed under high pressure and/or high temperature[7]. Similar reactions take place by irradiation of ultraviolet light even at low temperature[8].

Recently, it was reported that a new A1C60 phase was obtained by a solid-state reaction of a mixture of C60 powder and alkali metal in a sealed quartz capillary at high temperature[9], and also by a chemical reaction of toluene solution containing C60 and alkali metal chips in a solution cell at low temperature[10]. Several groups have reported that a compound of Rb1C60 has two stable phases and shows a first order structural phase transition at about 350 K[11-14]. Above 350 K the stable phase of Rb1C60 is fcc, while a body-centered-orthorhombic (bco) phase is stabilized below 350K. In the latter case, C60 molecules are linked by covalent bonds and form the polymeric phase. The Rb1C60 phase provides a structual transition driven by reversible

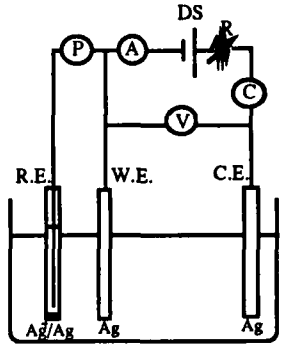
formation and breaking of covalent bonds. In the polymeric phase the distance between neighboring C60 molecules is 9.12 Å, of which the value is fairly smaller than that of the spacing in the usual fcc phase, 10.02 Å. Also, the bco RbiC60 is thought to be a quasi-one-dimensional metal accompanying with a Peierls transition at 50 K[15].

We developed an electrolysis process to get the polymeric RbiC60 film. In this paper the detailed conditions of the electrolysis are shown and fundamental properties of the obtained films are discussed.

EXPERIMENT

Figure 1 shows the used experimental electrolyte cell for the synthesis of the AxC60 film. The anode and the cathode were silver plates and the reference electrode was Ag/Ag^+. The electrolyte solution was a mixture of 0.3mM-C60, 0.1N-RbClO4 and dimetyleformuamide (DMF)/Toluene (1:1). The DMF and toluene were dried three times. The electric power was applied in a constant current mode to get a rapid reaction. The current density was about 0.5μ A/cm^2 where the maximum bias voltage was about 0.8 V. A reaction time was 10～200 hours. The reaction temperature (Tr) was changed from room temperature (10 ℃) up to 60 ℃.

The characterizations of the obtained films were done by reflected X-ray diffraction (XRD) ,Raman spectra, X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM).



0.3mM - C_{60} 0.1N-RbClO4 DMF/Toluene (1:1)
P:Potentiometer, A:Amperemeter,
DS: D.C.Power Source, R:Rheostat,
R.E.:Reference Electrode,
W.E.:Working Electrode,
C.E.:Counter Electrode, V:Voltmeter,
C:Voltameter,

FIGURE 1 Elecrolyte cell for the synthesis of the AxC60 Film.

RESULTS AND DISCUSSION

After the electrolysis, a black film was formed on the cathode and a yellowish film was formed on the anode. The color of the film deposited on the cathode varied with changing Tr. The film obtained at Tr of 10 ℃ was brown . The color of the film became darker and the film became thicker with increasing Tr. In the range of Tr's above 50 ℃ white

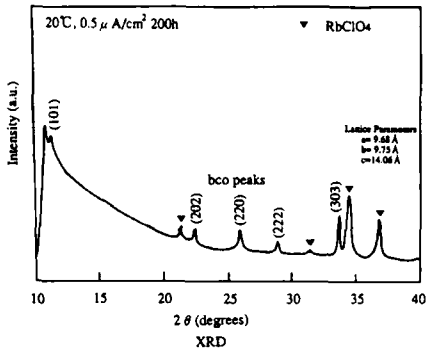


FIGURE 2 The XRD (CuK α) pattern of the as-prepared electrolysis AxC60 film.

materials adhered on the cathode surface and the film became gray. On the other hand, the film on the surface of the anode was thin and the color didn't almost change with increasing Tr.

Figure 2 shows the typical XRD pattern of the electrolysis film which was prepared with the conditions: Jd=0.5 μ A/cm^2, Tr=30 ℃ and a reaction time of 10 hours. The diffraction pattern indicated that the obtained film was a body-centered orthorhombic (bco) phase. In Fig.3 the major peaks of the bco phase are shown for the as-prepared film (a), the film rinsed by ethanol after the preparation (b), the film annealed after the rinsing in a vacuum at 150 ℃ for 10 h and slowly cooled (c). The bco phase was maintained and the lattice parameters slightly changed by the above stated treatments. The value of lattice parameters of a or b was smaller than that of c by about 1 Å. The obtained results reveal that the prepared film has the polymeric phase similar to the phase previously reported with respects to the Rb1C60.

The effect of the polymerization on vibration modes of solid C60 has been studied by Raman spectra. Figure 4 shows the Raman data of the following films: (a) an evaporated C60 film, (b) the as-prepared electrolysis film, (c) the ethanol-rinsed film after deposition, and (d) the annealed film after the rinsing. Since the impurities of the film were removed by the ethanol rinsing, the clear peaks of solid C60 were observed. The Raman spectra of the evaporated C60 film reveals a sharp peak of *Ag* mode (ca.1470cm^{-1}) which is in good agreement with the well known spectrum[16,17]. In the Raman spectra of the electrolysis film, the tangetial *Ag* mode was observed to soften

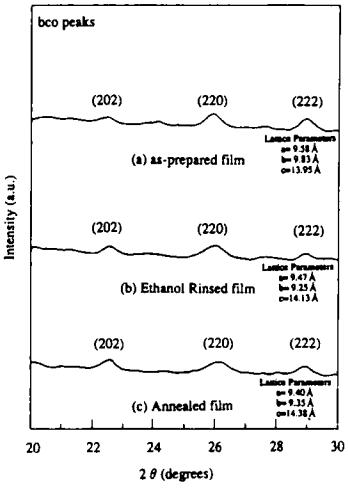


FIGURE 3 The XRD patterns observed in the as-prepared electrolysis film(a), the rinsed film by ethanol (b), and the annealed film (c).

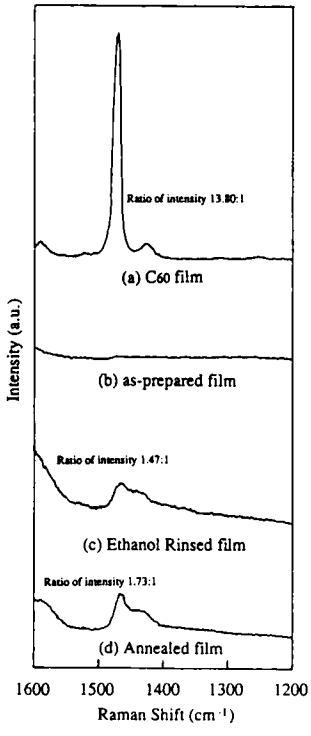


FIGURE 4 The Raman spectra observed in the evaporated C60 film (a), the as-prepared electrolysis film (b), the rinsed film (c), and the annealed film (d).

by about $10cm^{-1}$, similar to that observed in a photoinduced C60 polymer[8]. Furthermore, many new peaks downsifted for the *Ag* peak were also observed in the comparatively wide range of 1450～$1400cm^{-1}$, which can be attributed to a charge-transfer-induced elongation of the intramolecule bond length. These results indicate that the electrolysis film include C60 molecules in the polymeric phase.

Figure 5 shows XPS core spectra (C1s, Rb3d) of the evaporated C60 film and electrolysis films deposited at different Tr's. The binding energy of carbon of the electrolysis films were slightly smaller than that of the evaporated C60 film, which may be attributed to a change of an electron state induced by a charge transfer. The spectra were not significantly dependent on Tr. The observed spectra of Rb3d really indicates the existence of Rb ions in the electrolysis films.

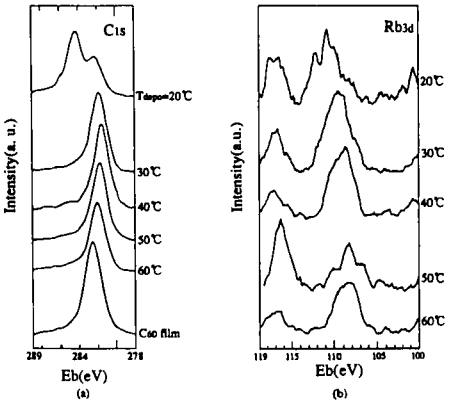


FIGURE 5 XPS core spectra of the evaporated C60 film, and the electrolysis films prepred Tr=20℃～60℃.

Figure 6 shows the SEM photographs of the films prepared by changing Tr. In the case of Tr=10 ℃, a remarkable change was not observed on the surface of the electrode. The characteristic microstructure of the film was found at Tr of ca. 20 ℃ and the particles in the film had a spindle-like shape. An anisotropic growth of particles was observed as increasing Tr, suggesting like an aggregated structure of C60 polymer. The length of the particles increased with increasing Tr as follows: 400 nm at Tr of 20 ℃, 800 nm at 30 ℃, about 1 μm at 40 ℃～60 ℃. In the case of Tr above 40 ℃ the length of the particles was almost constant. Conversely, the diameter became larger as increasing Tr, indicating that the growth of the particles shows two different modes for Tr. The thickness of

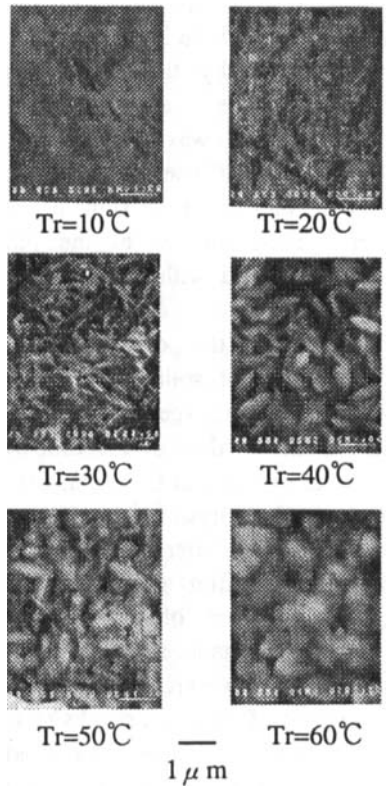


FIGURE 6 The SEM photographs of the surfaces of the films prepared at Tr=10℃～60℃.

the film increased with increasing Tr and the microstructure did not change. It should be noticed that the size of the particles was dependent on only Tr, but independent on the reaction time.

Obtained results strongly suggest that the electrolysis process may be used to get polymeric RbiC60 film on silver plates. The mechanism of the film deposition is not well clarified, but we think that the chemical reaction between $C60^-$ ions and Rb^+ ions on the cathode is essential for the electrolysis. The expected process of the electrolysis is schematically shown in Fig. 7. Several groups have reported that the valence of C60 molecules is changed by turns from 0 to -6 [18-20]typically at -0.82, -1.26, -1.82, -2.33, -2.89, -3.34V vs Fc/Fc^+ in an organic electrolyte solution. So $C60^-$ ions are formed at bias voltage of about 0.8 V in the vicinity of the cathode. Then, the polymerization of C60 with alkali metal ions takes place in the organic electrolyte solution. The unsoluble products are deposited on the surface of the cathode to form the film.

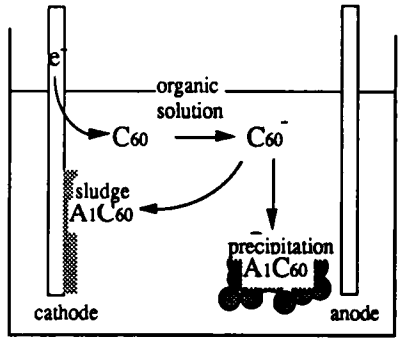


FIGURE 7 The schematic process of the electrolytsis for the synthses of the AiC60 film

SUMMARY

We succeeded for the first time in the synthesis of polymeric RbiC60 films on sliver plates by electrolysis where a mixtured solution of 0.3mM-C60, 0.1N-RbClO4 and DMF/Toluene (1:1) was used. The microstructure of the film indicates the characteristic growth of the particles. The reaction temperature Tr was an important parameter for the film deposition and the optimum Tr was about 30℃. The Raman spectra of the obtained films suggested the existence of solid C60 and revealed the features of the polymeric C60, of which the crystal structure was a body-centered-orthorhombic phase analized by X-ray diffraction. The more detailed characterization of the electrolysis film is the subject a for future studies.

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