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Preparation and characterization of C_{60} films on ionic substrates

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Abstract. Epitaxial (111)-oriented C_{60} films have been grown on the (100) surfaces of a few ionic substrates, such as KCl, KBr, NaCl and LiF, by physical vapour deposition, and have been characterized by SEM (scanning electron microscopy), XRD (x-ray diffraction), pole figures of XRD, Raman and Rutherford backscattering spectrometry (RBS). We have found that continuously and entirely (111)-oriented epitaxial C_{60} films can be grown on ionic substrates in a wide temperature range, 40 to 120 °C, and at very different deposition rates, from 1.5 to 35 Å min^{-1}. Single crystal and entirely (111)-oriented C_{60} films with grain size of 1 to 3 μm could also be grown at a relatively high temperature and low deposition rate, 120 °C, and 1.5 Å min^{-1}, respectively. Raman and RBS measurements show that the films have high quality without significant impurities. The optical property has also been measured in the UV–visible region, and the optical band gap has been determined to be 1.74 eV.

1. Introduction

A great attention has been paid to fullerene and its derived materials since the discovery of C_{60}, particularly the macroscopic quantity synthesis method and superconductivity and other fascinating properties of C_{60} [1, 2]. Since high quality films can play an important role in furthering understanding of fullerene and fullerene derived materials, a great number of studies have been conducted on C_{60} epitaxial film growth on different types of substrate, such as metals [3–5], ionic crystals [6–9], semiconductors [10–13] and layered materials [6, 7, 14, 15]. The growth of C_{60} film is not sensitive to layered substrate due to the weak van der Waals interaction between C_{60} molecules and the substrate, and large (111)-oriented C_{60} single crystals have already been formed on layered substrates, such as MoS_2 [16] and GeS [13]. Single crystal C_{60} grains have also been formed on metal [17, 18] and semiconductor [19] substrates. C_{60} film growth on ionic crystals, such as KCl [20], KBr [20, 21], NaCl [20] and KI [22], has also been performed intensively as there are several advantages [7]. However the strong electromagnetic interaction of C_{60} molecules with the substrate and the large lattice mismatching make it very difficult for C_{60} grains to grow in a preferred orientation [7, 22]. Although epitaxial C_{60} films have been already grown on alkali halide substrates, weak epitaxial character was observed and coexistent fcc and hcp structures were found [7]. At the same time, low deposition rate, as low as 0.4 to 5 Å min^{-1}, [7, 20, 22] ($\ll$ monolayer min^{-1}) has been used extensively in the C_{60} film growth on most of substrates to obtain epitaxial films. It was claimed that at an appropriate

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low deposition rate the deposited molecules could afford to settle at such a stable position having weaker interaction with the substrate [22]. However the low deposition rate makes C_{60} film preparation really time consuming. We have reported our successful preparation of C_{60} films on alkali halide substrates [23]. In this paper, we will extend on the preparation and characterization of C_{60} film growth on ionic substrates. The optical measurement in the UV–visible region and optical bandgap value of these high quality C_{60} films will be also reported.

2. Experiment

C_{60} films were prepared in an ultra-high vacuum (UHV) molecular beam epitaxy (MBE) system by sublimation under a base pressure of 10^{-7} Pa. High purity C_{60} (99.8%) powder was used for evaporation. A small amount of C_{60} powder was placed in a graphite boat and kept at 300 °C for several hours for degas, and then the powder was kept in high vacuum. During the growth, the substrates, freshly cleaved ionic substrates, were kept at different temperatures from 40 to 250 °C for different samples. Above 250 °C, the resublimating of C_{60} on substrates was becoming significant. The substrate was firstly heated at 500 °C for 1 to 2 hours to clean the substrate surface under 10^{-7} Pa. At the same time, the temperature of the C_{60} source was increased to 300 °C and maintained for 1 to 2 hours for preheating to obtain a stable deposition rate in the later deposition process. The substrate temperature was then decreased to the expected deposition temperature. Thereafter, deposition at very low deposition rate began with the shutter of the C_{60} source open. The deposition rate in this process was very low, in total 2 or 3 monolayers for 1–2 hours. Finally a higher deposition rate, from 1 to 35 Å min^{-1} by changing the source temperature from 300 to 550 °C, were used to get a film with expected thickness. After the deposition the temperature of substrate was decreased to room temperature gradually. Film thickness was monitored by a quartz crystal microbalance.

The film structure were then characterized by XRD and XRD pole figures in air by an X'Pert–MRD x-ray analytical instrument from Philips Company. The peak position, intensity and full width at half maximum (FWHM) was obtained by fitting the XRD spectra using a Gaussian function. A JEOL (Japan Electronic and Optical Laboratory) Superprobe733 electron microscope was used for film morphology measurement. Prior to SEM measurement, a layer of gold with thickness of 25 nm, was deposited on C_{60} films to prevent charging up. During experiment, the accelerated voltage of the electron beam is 15 keV. A micro-Raman system was used to characterize the C_{60} films too. RBS was used to determine the thickness of the films. 2.0 MeV He^+ ions incident on the sample at normal direction were employed for RBS analyses, and the backscattering ions were detected at 165°. The RBS spectrum simulation program RUMP [24] was used to obtain the atomic fraction and thickness of all films. The thickness from RUMP simulation was then used to calculate the absorptivity of the films from the absorption measured in the optical transmission spectra, and thus determine the optical band gap. The optical transmission spectra were detected by a microscope photometer in the wavelength region from 230 to 800 nm.

3. Results and discussion

Figures 1(a) and 1(b) show the surface morphology of a typical film on KCl(100) deposited at substrate temperature of 120 °C and deposition rate of 1.5 Å min^{-1} with small and large magnifications. The film thickness is approximately 1760 Å. Figure 1(a) shows the film is rather smooth and continuously grown, and figure 1(b) shows that the film is composed of

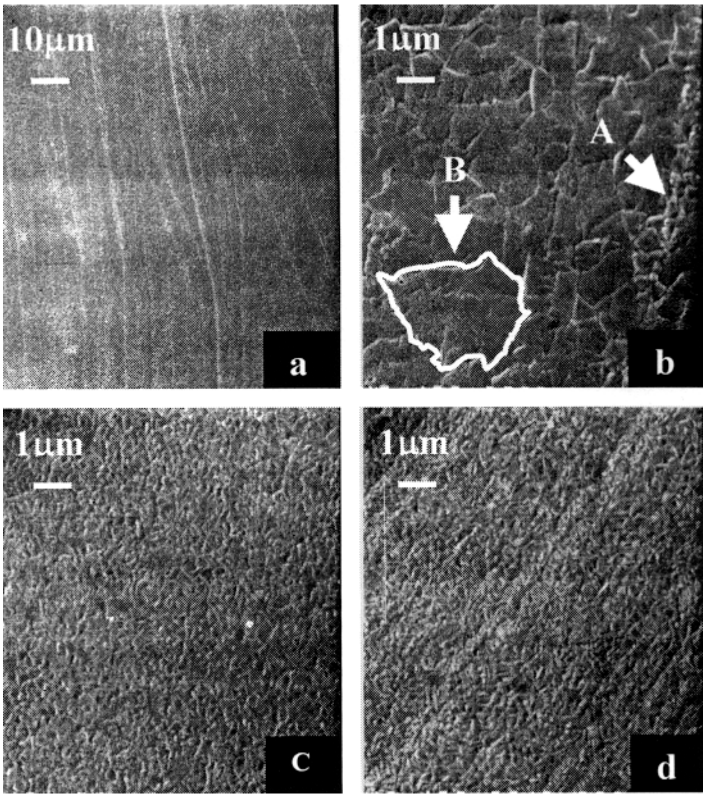

Figure 1. (a), (b) are SEM images of a C_{60} film deposited at substrate temperature of 120 °C and deposition rate of 1.5 Å min^{-1} with small and large magnification. The film thickness is approximately 1760 Å. Figures 1(c) and 1(d) are images of the films deposited at very high deposition rate (substrate temperature, 120 °C and deposition rate, 35 Å min^{-1}), and very low substrate temperature (substrate temperature, 40 °C and deposition rate, 1.5 Å min^{-1}).

many single crystal grains arrayed tightly with sizes approximately of 1 to 3 μm. The pattern in figure 1(a) is due to the cleavage of substrate KCl. 'A' in figure 1(b) shows the cleavage edge of the substrate, KCl, and 'B' shows a single crystal C_{60} grains with a size of approximately 3 μm. The morphologies of two films deposited under two extremely different conditions are also shown in figures 1(c) and 1(d). Figures 1(c) and 1(d) show the films deposited at very high deposition rate (substrate temperature, 120 °C and deposition rate, 35 Å min^{-1}), and very low substrate temperature (substrate temperature, 40 °C and deposition rate, 1.5 Å min^{-1}) for comparison. We can see clearly from figures 1(c) to 1(d) that these two films are also continuously grown and composed of very small grains.

Figure 2 shows the 2θ–θ scan of the same C_{60} film on KCl(100) substrate as in figures 1(a) and 1(b). The inset is the Bragg peak of $C_{60}(111)$. The figure shows only (hhh) orientation, and narrow full widths at half maximum (FWHMs), approximately of 0.245°, and high intensity of the peak, as high as 2184, suggest the film to have high quality. This indicated that real epitaxial (111) orientated film has been grown by this self-mediated growth technique. The lattice parameter of C_{60} films, obtained from the $C_{60}(111)$ peak position, 10.946°, is 14.05 Å, which is smaller than the bulk lattice parameter, 14.17 Å. This may be due to the large lattice mismatch between the C_{60} and substrate KCl.

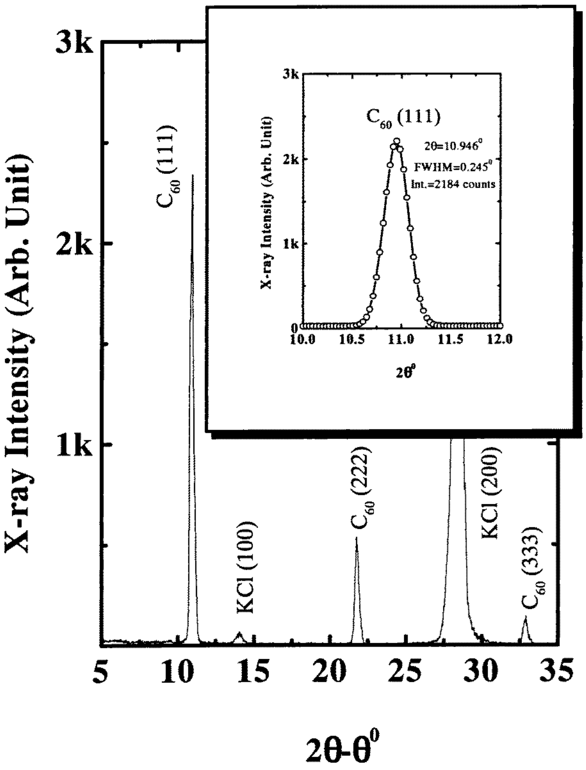

Figure 2. The 2θ–θ scan of the same C_{60} film as in figure 1(a) and 1(b). The substrate temperature is 120 °C and the thickness of the film is around 1760 Å. The deposition rate for this film is around 1.5 Å min^{-1}. The inset is the Bragg peak of C_{60}(111).

The 2θ–θ scans of the samples prepared at different substrate temperature from 40 to 250 °C, with the same source temperature of 450 °C, are shown in figure 3. The thickness of the all films is about 1500 Å, and the deposition rate for these films is the same, around 1.5 Å min^{-1} for comparison. It indicated that the entirely (111) orientated epitaxial films can be grown by the MBE technique at a rather low but wide temperature range, 40 to 120 °C, by using a self-mediating C_{60} layer. The films prepared at higher temperatures, 200 and 250 °C, show a (220) peak, indicating the films are polycrystalline, not epitaxial growth.

Films deposited at different deposition rate were also studied by XRD. Figure 4 shows the 2θ–θ scan of the films prepared at source temperature of 450, 500 and 550 °C, correspondingly the deposition rates are 1.5, 7 and 35 Å min^{-1} respectively. The substrate temperatures for all these films are 120 °C, and the thickness of all films is approximately 1500 Å. This figure shows only (hhh) orientations in spite of quite different deposition rates, and the intensity ratios of (111)/(222)/(333) for all three films are the same. This indicates that only the early stage of C_{60} growth was very important to prepare entirely (111) oriented epitaxial C_{60} film, and a later high deposition rate does not affect film quality heavily as reported by Yanagi and Sasaki [22] for the film grown on KI(001) substrates. They concluded that at an appropriate low deposition rate the deposited molecules could afford to settle at a stable position. This suggest the strong C_{60} molecule–substrate interaction is limited only to several monolayers from the

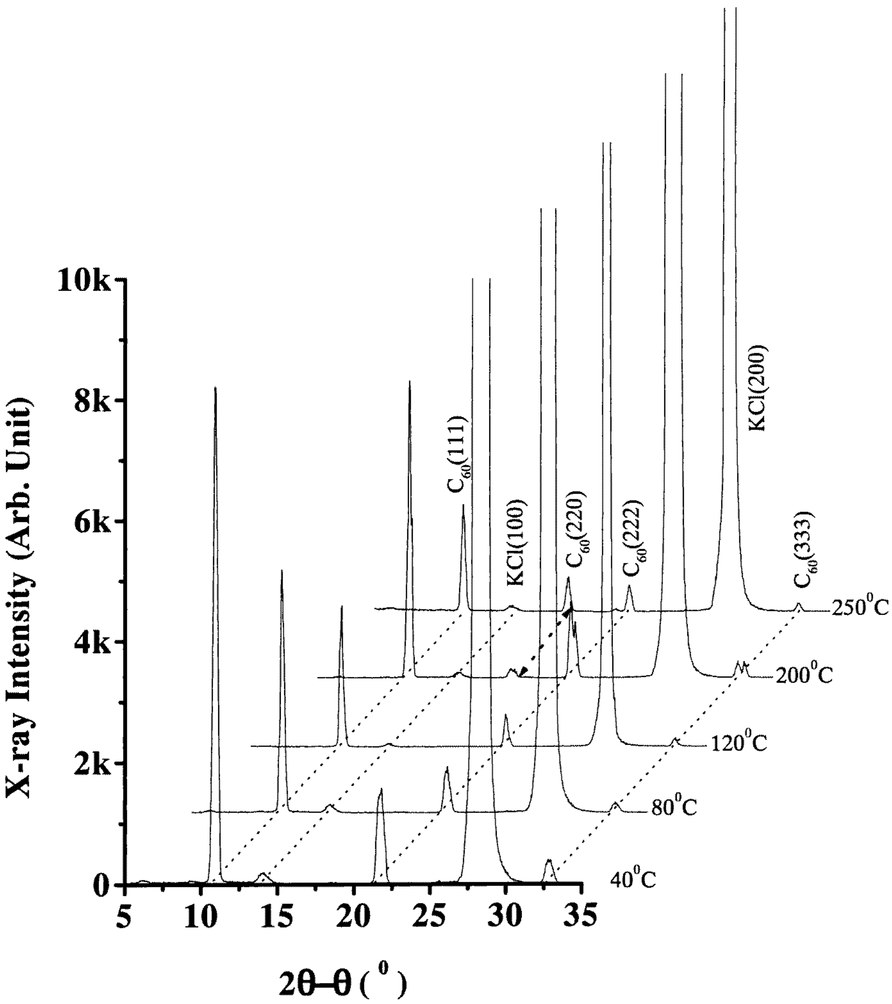

Figure 3. The 2θ–θ scan of the samples prepared at different substrate temperatures 40, 80, 120, 200 and 250 °C. The source temperatures were kept the same, 450 °C, so the deposition rates were the same, around 1.5 Å min^{-1}. All films are approximately 1500 Å.

interface of the C_{60} film and substrate; a later high deposition rate after several monolayers does not affect film quality critically.

Figures 5(a), 5(b), 5(c) and 5(d) show the rocking curves (θ scan at a certain 2θ angle) of substrate KCl(100), the main plane (111) of C_{60} film and two inter planes (220) and (311) of the same sample as in figures 1(a) and 1(b). The FWHM of the KCl(200) rocking curve is 0.176. The analysis of the rocking curve of C_{60}(111) shows a even narrower FWHM of 0.158; however the rocking curves of two inter planes (220) and (311) show wider FWHMs, 0.458 and 0.452 respectively. The sharp and strong rocking curve of C_{60}(111) implies that all the (111) planes are nearly well aligned. The wider and weak rocking curves of inter planes (220) and (311) suggest that the film is composed of many grains.

Figures 6(a) and 6(b) show pole figures of (220) and (311) inter planes of the same film as in figures 1(a) and 1(b). The pole figures were obtained by performing both φ and ψ scanning

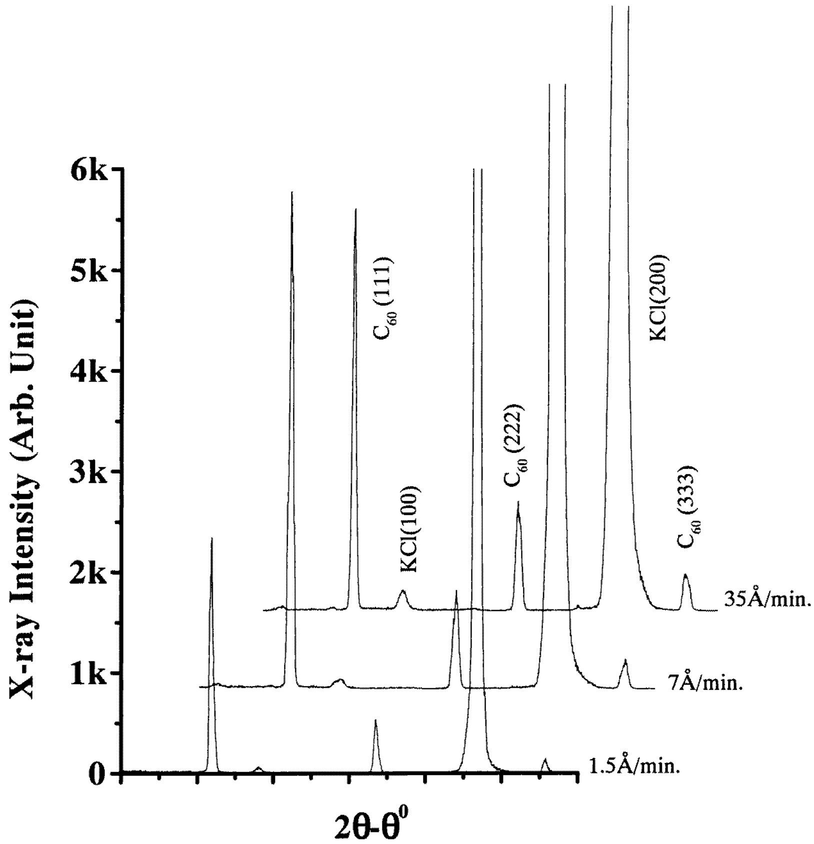

Figure 4. The 2θ–θ scan of the samples prepared at source temperatures of 450, 500 and 550 °C, correspondingly the deposition rates are 1.5, 7 and 35 Å min^{-1} respectively. The substrate temperature for all film preparation is 120 °C, and the thickness of all films is approximately 1500 Å.

in steps of 5 and 2° respectively. We can see that although the film is entirely (111) orientated, inter plane pole figures show twin structure. This is because there are many single crystal grains in the C_{60} films.

Epitaxial (111)C_{60} films have also been prepared on other ionic substrates, such as KBr, NaCl etc. Figure 7 shows the 2θ–θ scan of C_{60} film prepared on KBr at a source temperature of 450 °C, and the substrate temperature of 120 °C. The thickness of the film is 1500 Å, and the deposition rate for this film is around 1.5 Å min^{-1}. It indicated that epitaxial C_{60}(111) film on other ionic substrates could also be grown using the three-step process. The inset shows the rocking curves of C_{60}(111) with FWHM of 0.282 and intensity of 1072. The sharp and strong rocking curve of C_{60}(111) implies that all the (111) planes are fairly well aligned on the KBr substrate too. Therefore the C_{60} film growth is not sensitive to the lattice parameter too, even in the case of alkali halide, on which a stronger interaction between C_{60} and substrate exist compared to the layered substrates.

The Raman spectrum of a typical C_{60} film is shown in figure 8. The figure shows a very prominent peak at around 1470 cm^{-1}, characteristic of C_{60}. The low noise and relatively high intensity of the peak show the film is of high quality too.

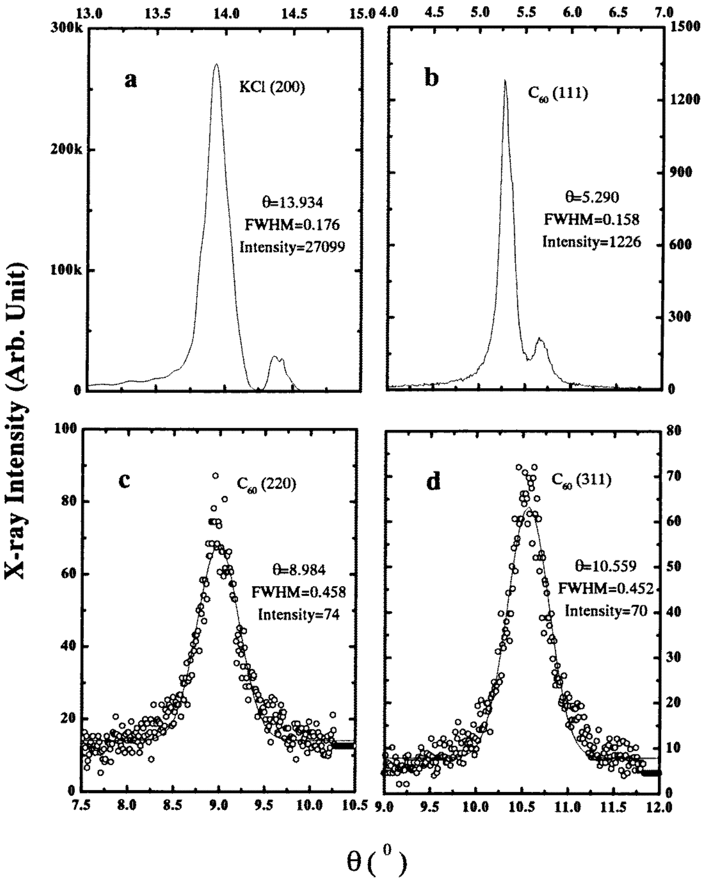

Figure 5. (a)–(d) The rocking curves (θ scan at a certain 2θ angle) of substrate KCl(100), main plane (111) and two inter planes (220) and (311) of the same sample as in figures 1(a), 1(b) and 2.

Figure 9 shows the RBS experimental and simulated spectra by RUMP of a typical C_{60} film prepared on KCl substrates. The simulated result shows that the thickness of the film is 500 nm that is around two times larger than that measured by a quartz crystal microbalance in the chamber. The thickness measured by the ion transmission method (not shown here) shows a similar result, that the measured thickness is around two times larger than that measured by quartz crystal microbalance. The spectrum does not show any significant impurities in the film.

Figure 10 shows the plot of absorption (solid circle) and $(\alpha/h\nu)^{1/2}$ (open circle) as a function of wavelength (photon energy $h\nu$) for the film prepared on KCl substrate at 120 °C by a deposition rate of 1.5 Å $\min^{-1}$. The thickness of this film is approximately 1760 Å. The inset shows the extrapolation to the curve of $(\alpha/h\nu)^{1/2}$ as a function of photon energy $h\nu$, and we obtain the optical band gap 1.74 eV. We observe four characteristic absorption structures at 2.74 eV, 3.93 eV, 4.64 eV and 4.90 eV, which agree with the four characteristic absorption structures as reported. However compared to their reported value 2.72, 3.61, 4.65 and 5.68 eV, we can see the second one shifted to higher energy, and the last one shifted to lower energy. These energies correspond to band to band transitions deriving from the corresponding molecular orbitals. Because C_{60} is in the form of solid films, an interesting example of a molecular solid in which both intra-molecular and solid state effects are important, the optical

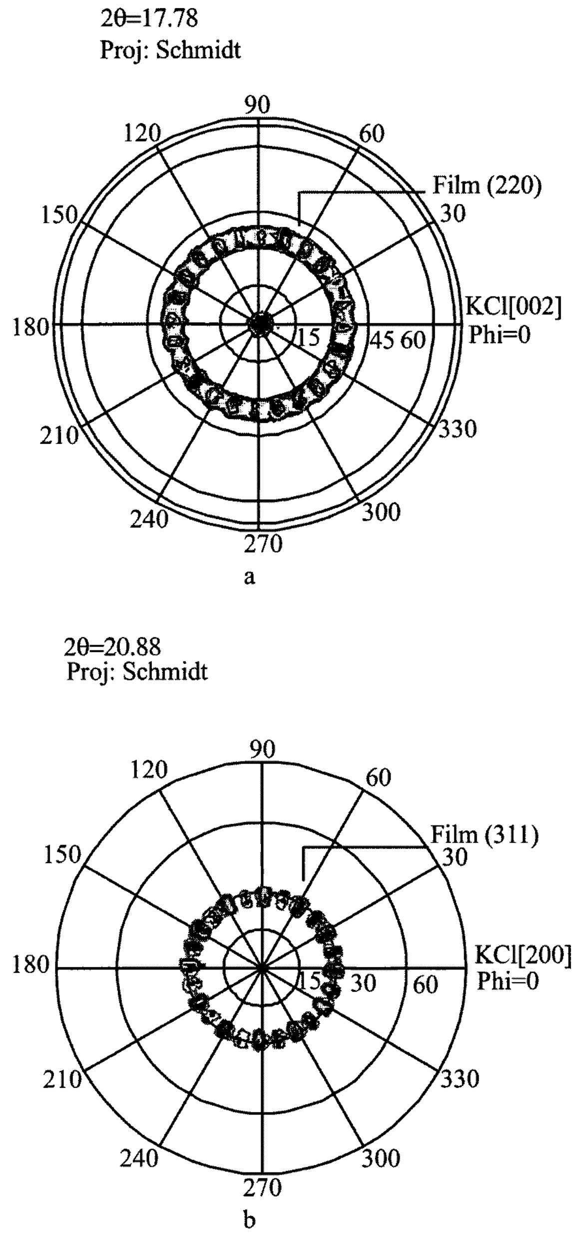

Figure 6. (a), (b) Pole figures of (220) and (311) inter planes of the same film as in figures 1(a), 1(b), 2 and 5. The pole figures were obtained by performing both φ and ψ scanning in steps of 5 and 2° respectively.

property of C_{60} films can be deeply influenced by the deposition conditions and by impurities or disordered structures. That is possibly the reason the shifts come out. We have also used the same method as Skumanich *et al* [25] to obtain the optical band gap of the C_{60} film by extrapolating the curve of $(\alpha/h\nu)^{1/2}$ (open circle) as a function of photon energy $h\nu$, and the optical band gap by this method is approximately 1.74 eV.

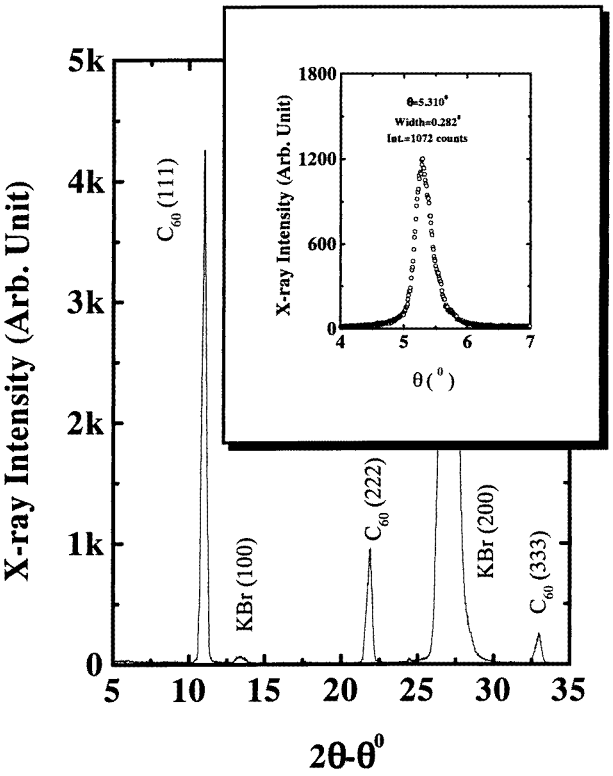

Figure 7. The 2θ–θ scan of the film prepared on KBr at a source temperature of 450 °C, and the substrate temperature is 120 °C. The thickness of the film is 1500 Å, and the deposition rate for this film is around 1.5 Å $\min^{-1}$, a rather low rate. The inset shows the rocking curves of C_{60}(111) of the sample film.

4. Discussion and conclusion

The SEM morphologies of the typical C_{60} films show very smooth surface in the cases of both low and high temperatures and both high and low deposition rates. However epitaxial C_{60} films with larger crystal grains were only obtained at low deposition rate and relatively high temperature. This suggest that although the strong interactions between C_{60} molecules and the ionic substrates are only limited to several monolayers, the lower deposition rate and high substrate temperature can still play a positive role in the film growth. Further XRD analysis shows that the films are completely (111) oriented, and the high intensities with narrow FWHM show the high quality of the films. Anyway the relatively high temperature induces both (111) and (110) orientations, and this indicates that C_{60} molecules at high temperature may have too much energy, so make C_{60} molecules orient randomly. RBS analyses show the film does not have any significant heavy impurities, and the Raman spectrum indicated a prominent C_{60} peak. The low background and high intensity of the peak show the film to have high quality too. The lattice parameter of C_{60} films, obtained from the C_{60}(111) peak position, 10.946°, is 14.05 Å, which is smaller than the bulk lattice parameter, 14.17 Å. Although the strong interactions between C_{60} molecules and ionic substrates are only limited in several monolayers, the large

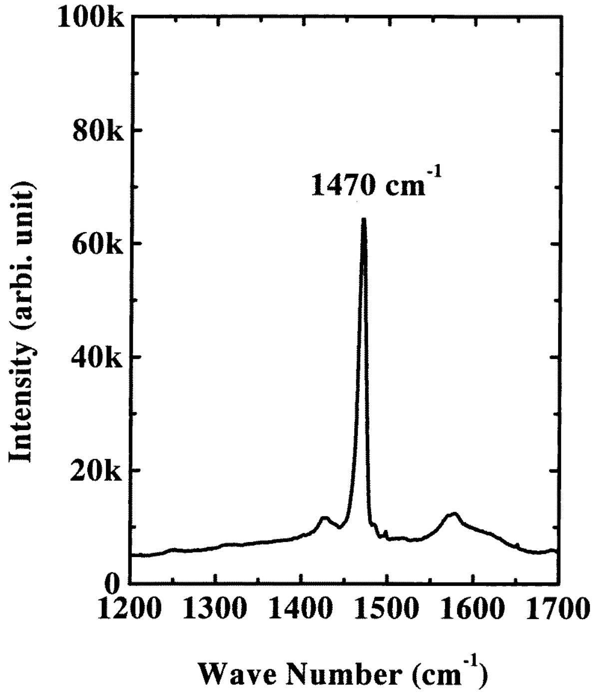

Figure 8. The Raman spectrum of a typical C_{60} film prepared at 120 °C.

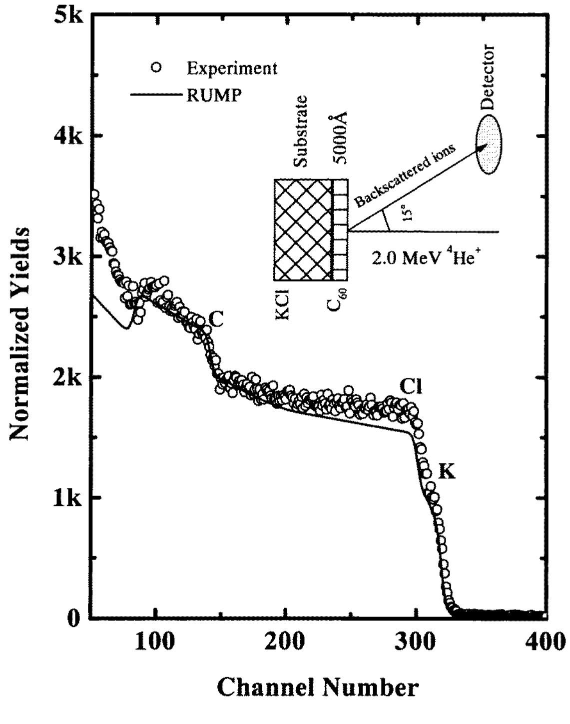

Figure 9. The Rutherford backscattering spectrometry of a typical C_{60} film prepared at 120 °C.

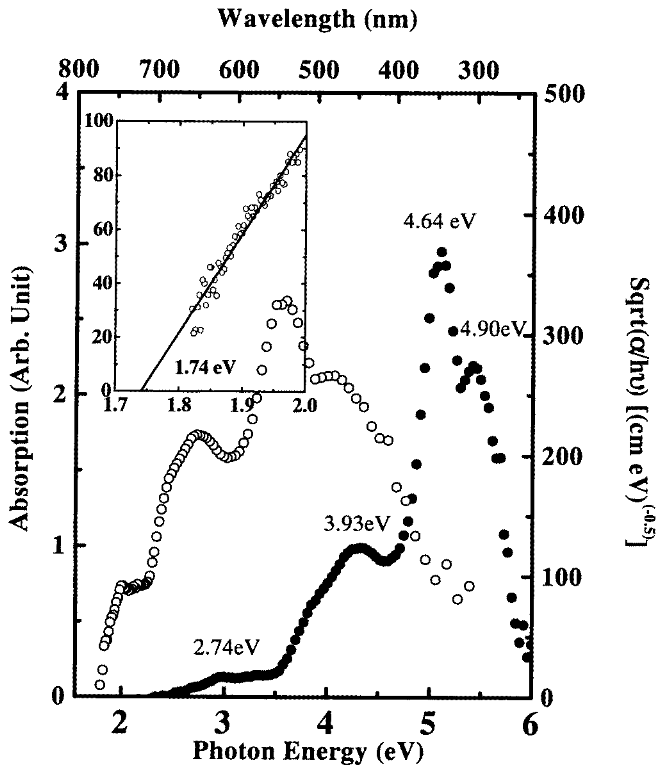

Figure 10. The plots of absorption (solid circles) and $(\alpha/h\nu)^{1/2}$ (open circles) as a function of photon energy $h\nu$ (wavelength) for the film prepared on KCl substrate at 120 °C by a deposition rate of 1.5 Å min^{-1}. The inset plot shows the extrapolation of the curve of $(\alpha/h\nu)^{1/2}$ (open circles) as a function of photon energy $h\nu$.

lattice mismatch between the C_{60} (14.17 Å) and substrate KCl (6.29 Å) still has a strong effect on the lattice parameter.

In conclusion, C_{60} films have been prepared on a few ionic substrates and characterized by SEM, XRD, XRD pole figure, Raman and RBS. The optical property has also been measured. It was found that continuously and entirely (111)-oriented epitaxial C_{60} films have been grown in a wide temperature range, 40 to 120 °C, and at very different deposition rates, from 1.5 to 35 Å min^{-1} by using two or three C_{60} monolayers grown at very low deposition rate as a self-mediating layer. We have also found single crystal $C_{60}(111)$ orientated films with grain size of 1 to 3 μm could be grown at a relatively high temperature and low deposition rate, approximately 120 °C and 1.5 Å min^{-1} respectively. RBS and Raman measurements confirm that high quality films without impurity have been prepared, and optical measurement in the UV–visible region shows the optical band gap is 1.74 eV.

Acknowledgment

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