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The nano-structure of C_{60} photopolymers has been investigated using *in situ* Fourier-Transform Infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). The FTIR and XPS studies revealed that the C_{60} photopolymer has a cross-linking via a [2+2] cycloaddition four-membered ring and formed a 2D rhombohedral structure when the polymerization was saturated. Using STM, we have successfully observed the direct real-space imaging of the C_{60} dimers and trimers in a C_{60} monolayer supported on a clean semiconductor surface.

Keywords: C_{60} photopolymers; nano-structure; FTIR; XPS; STM; tight-binding MD calculations

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INTRODUCTION

Recently, fullerene polymers have been designated as a new-form of carbon materials. Rao *et al.* first reported that C_{60} molecules are polymerized in a C_{60} film under irradiation using an Ar ion laser or UV-vis lamp[1]. Since then, there have been many reports on the synthesis of C_{60} polymers using various kinds of methods such as (1) photoirradiation[1], (2) high pressure and high temperature[2], (3) alkali-metal doping[3], and (4) mechanochemical reactions[4]. In spite of the fact that C_{60} photopolymers have been reported, their structural aspects such as cross-linking and polymer configuration remain unsolved. In order to elucidate the cross-linking and configuration of the C_{60} photopolymers, we have examined the photoirradiated C_{60} film in an ultrahigh vacuum (UHV) chamber using *in situ* high-resolution FTIR in combination with theoretical IR calculations based on a tight-binding method[5,6], XPS[7-10], and STM[11,12]. In this paper, our recent results on the nano-structure of C_{60} photopolymers obtained by these methods are presented.

EXPERIMENTAL

C_{60} powder was placed into a quartz crucible. Thereafter, the C_{60} films were formed on a CsI substrate at 373 K by sublimation at 673 K for 1.5 h in an UHV chamber. The thickness of the formed C_{60} film was estimated to be about 100 nm. UV-vis light from a 500 W mercury lamp (emission lines in the range 2-4 eV) was used for the photopolymerization. The intensity of this UV-vis light over a 50 mmϕ area was 3-4 W. Before and after the photoirradiation of the C_{60} film on the CsI substrate, the FTIR absorption spectra of the pristine and phototransformed C_{60} films were measured with the high resolution of 0.25 cm^{-1} at room temperature.

For XPS measurement, after the C_{60} film deposited on a gold-coated stainless steel substrate, this sample was taken out of the UHV chamber and introduced into the XPS apparatus (MgKα=1253.6 eV). It was confirmed that there is no effect of charge-up on the sample upon X-ray irradiation in the present experiments. The 500 W mercury (Hg) lamp was also used for the photopolymerization.

For STM measurement, an Ag-Si (111) substrate was prepared by depositing one monolayer of Ag onto a clean Si (111) surface[13]. The STM observations were performed at room temperature in a pressure of less than 1 x10^{-10} Torr before and after the photoirradiation of the C_{60} monolayer formed on the substrate.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum for the phototransformed C_{60} film after a 26-h irradiation at room temperature[5]. There are not only many new weak IR peaks but there is also peak splitting of the four intrinsic IR-active modes. In order to identify the C_{120} dimer structure, we examined the theoretical IR spectra of several C_{120} isomers (see Fig. 2) using the TB-MD method, and compared these with the experimental IR spectrum shown in Fig. 1. It was found that the theoretical IR spectrum of the dumbbell [2+2] C_{120} structure reproduces the present experimental IR spectra of the photopolymerized C_{60} films better than any of the other dimer isomers[6].

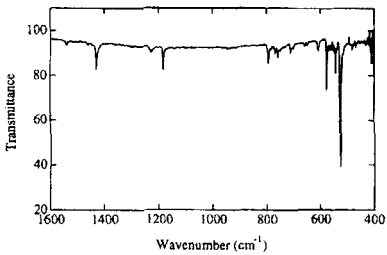


Fig. 1. FTIR spectrum for the phototransformed C_{60} film after 26-h irradiation using the 500W Hg lamp at 300 K.

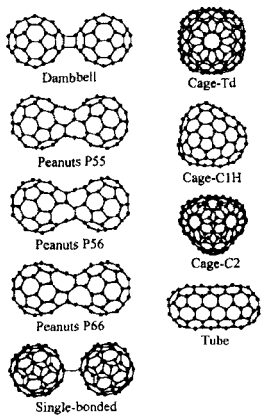


Fig. 2. Geometry of the nine possible C_{120} isomers.

From XPS measurments, we obtained Fig. 3 showing that the average number of photopolymerized C_{60} molecules increased with irradiation time and the photopolymerization was saturated after about 350-h of photoirradiation[8]. From the result in Fig. 3, the saturation number of the [2+2] four-membered rings formed on a C_{60} molecule was estimated to be approximately 6. What does this value imply? Based on the fact that photopolymerization proceeds via the [2+2] cycloaddition ring formation between adjacent C_{60} molecules[7,8], two possible configurations can be considered. One possible configuration is the 2D-rhombohedral structure and the other one is the 3D-octahedral structure, as shown in Fig. 4. In these figures, the designed atoms are those with intermolecular C-C bonds. In the present study, the pristine C_{60} film was deposited on a Au-coated stainless steel substrate. Previous work on C_{60} film growth by STM has shown C_{60} to exhibit a preference for the formation of close-packed hexagonal overlayers, a (111) fcc structure, on gold surfaces such as a polycrystalline gold substrate[14,15]. Consequently, it can be concluded that the 2D-rhombohedral structure is preferable than the 3D octahedral structure for the C_{60} photopolymer.

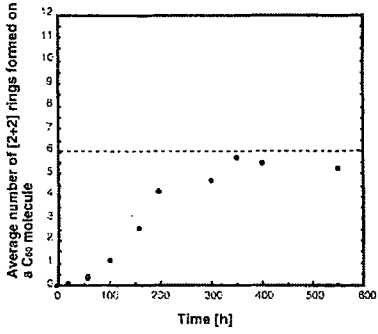
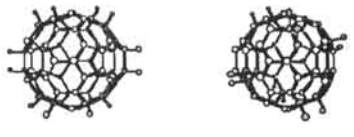


Fig. 3. The average number of [2+2] four-membered rings formed on a C_{60} molecule as a function of irradiation time.



(a) 2D-Rhombohedral (b) 3D-Octahedral

Fig. 4. Possible configurations of C_{60} polymers with six [2+2] cycloaddition four-membered rings formed on a C_{60} molecule: (a) 2D-rhombohedral and (b) 3D-octahedral configurations. The designed atoms are those including intermolecular C-C bonds.

Figure 5 shows the real-space imaging of the C_{60} monolayer on the Ag-Si(111) surface after a 100-h photoirradiation[12]. Because the unreacted C_{60} molecules can freely

rotate in three dimensions at room temperature, these molecules were observed as a white circle. On the other hand, because photoplymerized C_{60} molecules could not freely rotate, these molecules were observed as indicated by the open and closed arrows in Fig. 5. One can see that the open and closed arrows represent the STM images of the C_{180} trimers (a linear chain) and C_{120} dimers, respectively. From the STM images of the unreacted C_{60} molecules, the intermolecular distance was determined to be 1.016 nm which is in good agreement with that of 1.002 nm for the C_{60} single crystal[11]. This indicates that the interaction between the C_{60} molecules and the substrate is comparable to that between adjacent C_{60} molecules. Accordingly, the effect of the substrate on the C_{60} photopolymerization was negligibly small. Using the intermolecular distance between adjacent unreacted C_{60} molecules as a reference, we estimated the average C_{60}-C_{60} distance of the dimers to be 0.87 nm, which agrees well with that of 0.91 nm for the dumbbell-shaped C_{120} reported by Komatsu *et al.*[4]. On the other hand, the average distance of the C_{180} trimers was found to be 0.92 nm, indicating that the local structure of the trimers is somewhat different from that of the dimers.

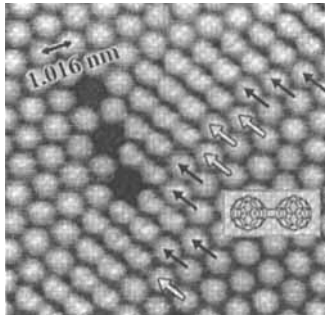


Fig. 5. STM image of a local nano-structure of C_{60} monolayer on $\sqrt{3}x\sqrt{3}$Ag-Si(111) surface after 100 h of UV-vis light irradiation. Open and closed arrows indicate C_{60} trimers and dimers, respectively. Unreacted C_{60} molecules were observed as a white circle.

SUMMARY

We have elucidated the nano-structure of a photopolymerized C_{60} film using *in situ* FTIR, XPS, and STM. Firstly, a comparison of the FTIR results with IR calculations

indicated that the C_{60} dimer has a relaxed structure (D_{2h} symmetry) via a [2+2] cycloaddition four-membered ring. Secondly, a change in the intensity of the C 1s shake-up satellite obtained by XPS showed that six [2+2] rings were formed on a C_{60} molecule when the polymerization was saturated. A possible configuration of the C_{60} photopolymer was 2D rhombohedral. Third, we observed direct real-space imaging of the C_{120} dimers and C_{180} trimers which were formed in a C_{60} monolayer supported on a Ag-Si (111) surface and obtained an intermolecular distance between adjacent C_{60} molecules of 0.87 nm for the dimer and 0.92 nm for the trimer. This discrepancy in the local nano-structure between the C_{120} dimer and C_{180} trimer was first observed using STM.

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