CHEMISTRY LETTERS, pp. 1905-1908, 1994.

Atomic Force Microscopic Observation of Plasma Polymerized Film. Hexamethylcyclotrisiloxane, Hexamethyldisiloxane, and Pyrrole as the Monomers

Michiko TAZAKI, Hiroyuki AIZAWA, and Terutake HOMMA*
Department of Chemical Process Engineering, Faculty of Engineering,
Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02

Atomic force microscopic observations of plasma polymerized thin films of the three monomers, hexamethylcyclotrisiloxane, hexamethyldisiloxane, and pyrrole, were made. The polymerization processes under fixed plasma conditions were followed with the reaction time. The differece of the polymerization rate between these monomers was clearly obtained by AFM observation.

Organic thin films coated on a suitable substrate can be obtained by plasma polymerization of low molecular weight organic compounds when they sublime at the plasma discharge. It is also recognized that the plasma polymerized films have flat surface and strong adhesive strength to the substrate.[1] These properties depend on the monomers used and the plasma discharge conditions.

Recently application of AFM(Atomic Force Microscope) to elucidate of the surface morphology of organic thin films is recognized.[2] However, little of the work for plasma polymerized films has been reported. The SEM observation, commonly used for the study of the surface morphology, has no surface sensitivity with poor resolution as is compared to the AFM, which means the difficulty might be encountered when the polymerized films are very thin. Here, we present AFM observation of plasma polymerized thin films obtained by three different monomers. It could be understood that the AFM observation of the films is useful when the AFM data are assisted by other conventional measurements such as SEM, FT-IR, and ESCA etc.

Three monomers, i.e., hexamethylcyclotrisiloxane(HMCTS), hexamethyldisiloxane(HMDS), and pyrrole, were used. The tubular reactor (I.D., 6 cm, length, 25 cm) with outer coil of capacitance coupling was used. The plasma discharge conditions were; 13.56 MHz, 30-55 Watts, pressure 0.6-0.8 Torr and argon gas flow rate of 10 ml/min(STP). Introduction of the monomer gases was regulated with the needle valve so that the total pressure in the reactor was maintained at the pressure through whole plasma discharge time. Several AFM (Seiko Instrument Inc. SPI3700/SPA-300) images for polymerized film from each monomers were obtained as a function of the discharge time. A mica surface was used for the supporter. Other measurements such as SEM, EDX, and FT-IR, were performed for characterization of the polymerized films, if necessary.

Figure 1 shows the AFM image of the 30 min polymerized film surface of HMCTS showing typical topogram. The mountain structure with high and low mountains is seen. The mountains are polymerized HMCTS because plain mica surface is quite flat as is seen in Fig.3. The height of low mountains seems to be almost less than 10 nm and almost 20 nm is for high mountains.

In order to check the film formation process of HMCTS, the AFM images of short plasma discharge time between 1 sec and 5 min were observed. Surprisingly, only time of 1 sec was enough to make the topogram similar to Fig.1 as is shown in Fig.2. However, if close look and a comparison between Fig.1 and Fig.2 are made, differences in the mountain heights and the shapes are clear. In Fig.2 there are sharper mountains with 40 nm height, and furthermore, the formation of very thin polymerized film on the supporter mica surface is also seen as vacancies in the mountains. Adding to these, the characteristic of this figure is the presence of many scratch lines on the vacant zones. The judgment of the presence of the thin film is made from the comparison of the cross-sectioned figures between Fig.2 and Fig.3. From these figures it can be understood that the growth of polymerized film is progressed as, initially sharper particles of the polymerized HMCTS are partially localized to decorate over the mica surface, then, with discharge time progress, the rest zones of low decoration are flattened by the polymerized HMCTS. Further prolongation of plasma discharge time, i.e., in 60 min there is flat polymerized surface with some amount of big mountains showing the heights approximately 200 nm. These observations indicate in plasma polymerization of HMCTS, the polymerized film is basically thickening with the flat surface. The film thickening was observed by weighing the polymerized film, too.

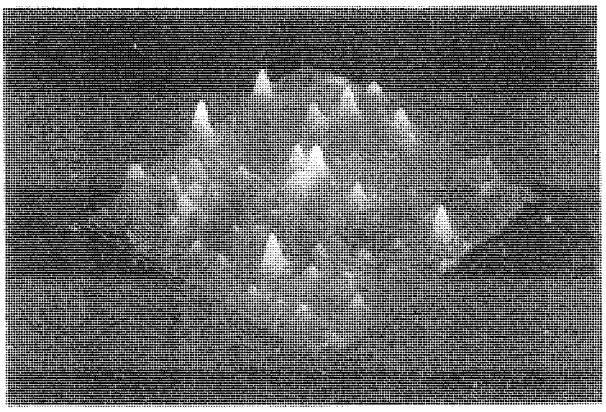

Fig.1. AFM image of plasma polymerized surface of HMCTS.
Polymerization time 30 min.
(abscissas: 5000 x 5000 nm)

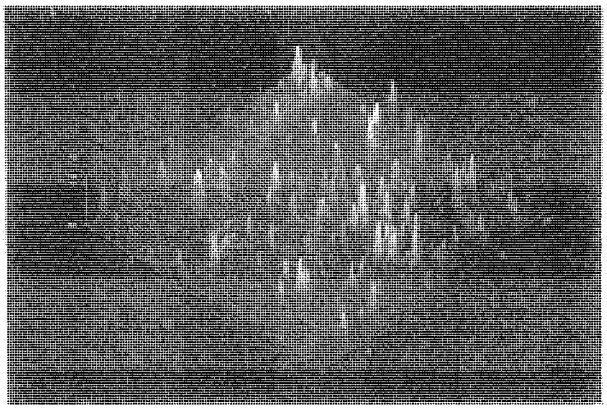

Fig.2. AFM image of plasma polymerized surface of HMCTS.
Polymerization time 1 sec.
(abscissas: 5000 x 5000 nm)

In spite of using the repulsive force mode of the AFM operation, where the cantilever tip contacts on the sample surface, there are no sweeping scratch lines on the surface in Fig.1. It shows the surface of polymerized film is rigid. It is well known that in plasma polymerized films dense network structure is exhibited. To certify this network structure, solvent swelling test by adding one drop of methyl ethyl ketone (MEK) on the surface of 30 min polymerized film was tested, since MEK can swell silicone rubber. After several minutes of evaporation of the solvent, imaging again showed no difference on the surface topogram.

Contrary to the polymerization behavior of HMCTS, different AFM images were obtained when HMDS monomer was used. The AFM images obtained at any plasma discharge time showed no clear topograms. However, after 30 min plasma discharge, growth of the polymerized thin film was identified by the FT-IR. Therefore, for this monomer, plasma polymerized film growth between 1 sec and 5 min discharge time was checked again. Initially, no presence of the polymerized film was obtained, however, after 5 min, the mica surface was thought to be covered with thin film which could be identified only by the increasing contact angle against water, though the AFM image was very flat. Reexamination of the AFM image has found the topogram as is shown in Fig. 4, in which approximately 1.5 nm of the mountain heights are apparent. Incidentally, it might be said that the contact angle method has very good surface sensitivity as has been described by IKADA et al.[3]

From this result, it was understood that the growth rates of plasma polymerized siloxane film have difference by the monomers, HMCTS and HMDS. This difference has been reported already by E.RADEVA et al.[4] In other words, in plasma polymerized siloxane films, to use of HMDS as the monomer means much flattened surface can be obtained than use of HMCTS.

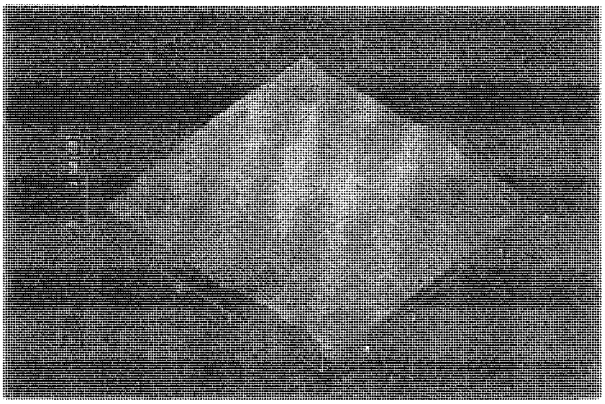

Fig.3. AFM image of cleavage surface of plain mica.
(abscissas: 5000 x 5000 nm)

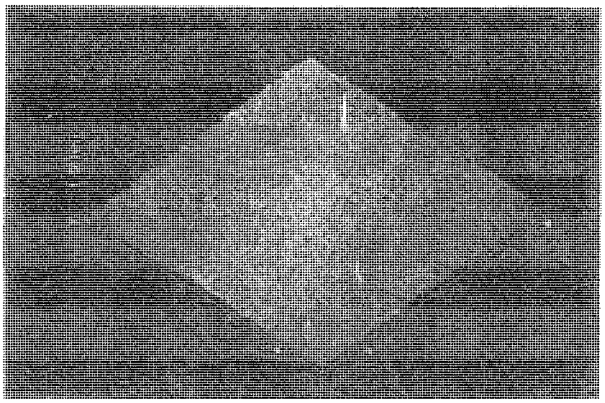

Fig.4. AFM image of plasma polymerized surface of HMDS.
Polymerization time 5 min.
(abscissas: 5000 x 5000 nm)

In plasma polymerization film of pyrrole, it was possible to obtain AFM images easily compared to that of HMDS. Pyrrole can be plasma polymerized with rather high film growth rates. From the AFM images taken at intervals of the plasma discharge time between 1 sec and 60 min, we could observe the same process of the film formation as described for the plasma film growth of HMCTS.

From the AFM observation of plasma polymerized films of these three monomers, our general understanding in growing of the surface structure of the plasma polymerization is building of the quite flat surfaces. This flattening would be caused by polymerization of monomers on the surface where the active sites for propagation of chains are located. If the polymerization is proceeded in the plasma gas phase and then, the polymerized particles would dropped on the substrate surface, it is hard to think of the building of such very flat surface. The CAP mechanism now prevailing in plasma polymerization accesses both polymer abolation and polymer formation. This mechanism is also to be considered for the flattening process.

Sometimes, as SEM images often show, the discrete big polymerized particle presented on the surfaces. These particles, contrary to the flat surface, seems to be growing in the plasma vapor phase and then deposit on the surface.

In summary, AFM observation gives further detailed information for the formation process of plasma polymerized thin films where especially the SEM observation is failed out.

References

1) H.Yasuda, " Plasma Polymerization," Academic Press, New York (1985).
2) N.Yoshino, *Chem. Lett.*, **1994**, 735.
3) Y.Ikada, T.Matsunaga, and M.Suzuki, *Nippon Kagaku Kaishi*, **1985**, 1079.
4) E.Radeva, D.Tsankov, K.Bobev, and L.Spassov, *J. Appl. Polym. Sci.*, **50**, 165 (1993).

(Received June 16, 1994)