TEM and TED Observations of Carbon Films Produced by Plasma CVD of Propane Gas

by
Yukio ICHINOSE, Fumiki IYAMA and Yoshihiko HIROTSU
Technological University of Nagaoka
1603-1, Kamitomioka-cho, Nagaoka,
Niigata 949-54, JAPAN

Abstract, Crystal structures of carbon films deposited by plasma CVD technique of propane gas was investigated. Several kinds of structures, pseudo-polmer, graphite, perfectly <001> oriented graphite and pseudo-diamond, were formed, which were dependent on the deposition temperature and the plasma CVD technique.

I. Introduction

We are at present interested in and investigating on processing amorphous and crystalline carbon films by means of the plasma CVD technique of propane gas. Based on TEM and TED studies, it was found that such phases as pseudo-polymer, polycrystalline graphite, fcc carbon and pseudo-diamond are formed in relation to the deposition temperature and the experimental technique. Some of these results were talked at the San Diego and the Bordeaux conferences.[1,2] By the inductance-type technique, the pseudo-polymer phase is formed at substrate temperatures of room to 200℃ and graphite phase appears at temperatures between 300 and 500℃. On the other hand, by the capacitance-type technique, graphite phase appears from room temperature to 200℃, and the perfectly <001> oriented graphite and the pseudo-diamond phases co-exist at temperatures between 300 and 450℃.

Such experimental results will be reported in details in the following.

II. Experimental Procedures

The two types of plasma CVD apparatus, as seen in Fig.1, were set up for the synthesis of carbon films by using propane gas. One is an inductance-type apparatus and the other a capacitance-type. The electric power source has a R.F.frequency of 13.56MHz with a maximum output of 1KW. These reaction chambers were evacuated to 10^{-6} Torr., followed by the introduction of the propane gas. The substrate temperatures for the carbon deposition ranged from room temperature to 500℃. It is expected that the efficiency of supplied power in obtaining high plasma density and temperature differs in the inductance- and capacitance-types. The latter is hopeful for synthesizing a diamond film because of a dense electric power in the space among both electrodes. The deposited carbon films were optically and structurally investigated by means of infrared spectroscopy and high resolution electron microscopy.

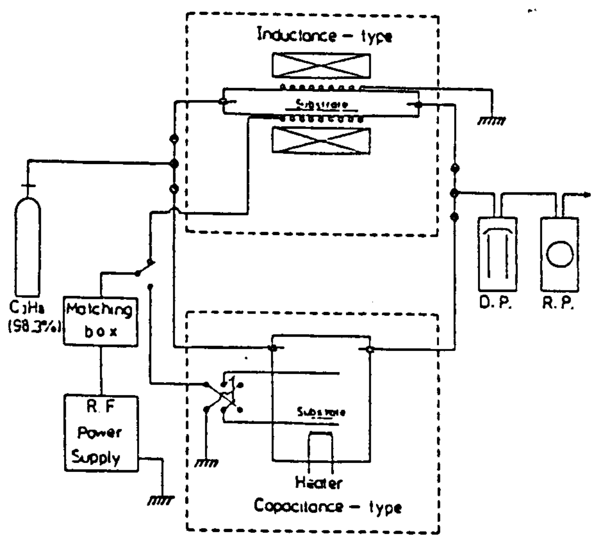

Figure 1. Plasma CVD apparatus.

III. Results

The carbon films obtained have various colors depending on the substrate temperature and the deposition technique. Figure 2 shows the substrate temperature dependence on the types of color. For example, in the case of capacitance-type, color varies from yellow to brown by the

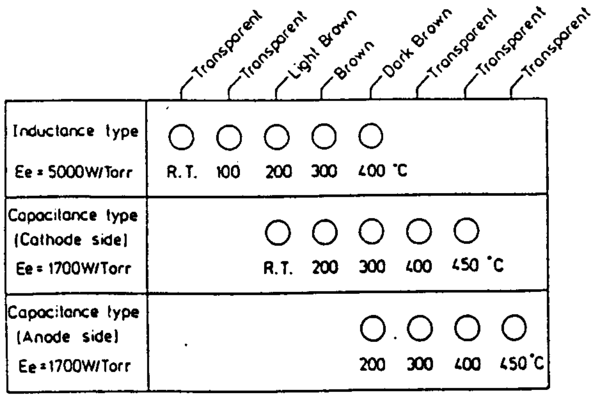

Figure 2. Classification of film colors.

substrate temperatures from room to 200-300℃, and transparent films were obtained at temperatures higher than 300-400℃. On the other hand, in the case of inductance-type, the order of color variation shifts to the high temperature side.

The transparent carbon film formed at room temperature by the inductance-type technique has a hydrogenated amorphous carbon structure, which is named pseudo-polymer.[2)] The transparent film formed at temperatures higher than 300℃ by the capacitance-type technique was found to have both structures of fcc carbon and diamond. The films being yellow to dark-brown in color were found to have both graphite and amorphous carbon structures. In this report, the results observed in the films deposited by the capacitance-type technique will be mainly presented. Figure 3 shows the infrared absorption spectra taken from the

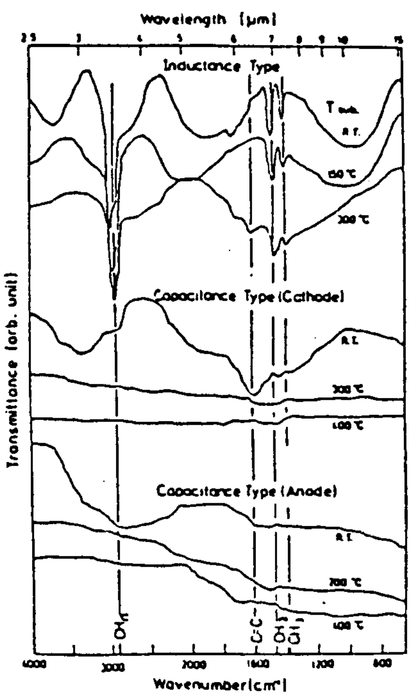

Figure 3. Infrared absorption spectra.

carbon films. Absorption at wavelength of 2900cm^{-1} does not appear in the films deposited by the capacitance-type technique, but all the films made by the inductance-type apparatus show absorption peaks at this wavelength, meaning the inclusion of large amounts of hydrogen atoms. Absorption at 1600cm^{-1} is due to carbon bondings of graphite structure. Films made by the capacitance-type technique lose the absorption spectra at this wavelength as the deposition temperature increases, which means the formation of non-graphite carbon films.

Structural characteristics of the transparent carbon films deposited at temperatures higher than 300℃ by the capacitance-type technique were studied by the TEM and TED techniques. As the results, four types of carbon structures were revealed: they are amorphous, randomly oriented graphite, uniaxially oriented graphite and pseudo-diamond structures.

Photo 1 shows an example of a TEM image and the corresponding halo-TED pattern of the amorphous carbon film.

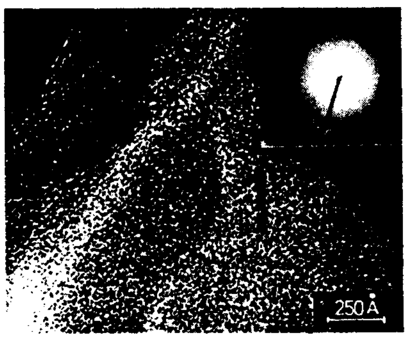

Photo 1. TEM and TED of amorphous carbon.

In Fig. 4 are shown an example of the TED pattern and a relation of the reflection intensity vs the inverse of interplaner spacing (1/d) of randomly oriented polycrystalline graphite. Solid lines show observed intensities and dashed ones are calculated intensities. The positions and intensities of the observed reflections agreed well with a calculated ones.

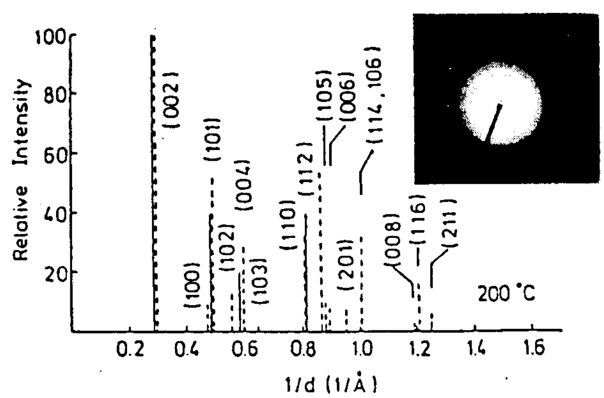

Figure 4. Reflection intensity versus 1/d of graphite.

In Fig. 5, an example of TED pattern and the observed reflection intensity vs 1/d are shown for uniaxially oriented graphite. The orientation axis was found to be <001> of graphite. Solid lines (observed intensities) and dashed lines (calculated ones) agreed well. We frequently observed the uniaxially oriented graphite and the pseudo-diamond structures co-existing in the same transparent carbon films deposited by means of capacitance-type technique.

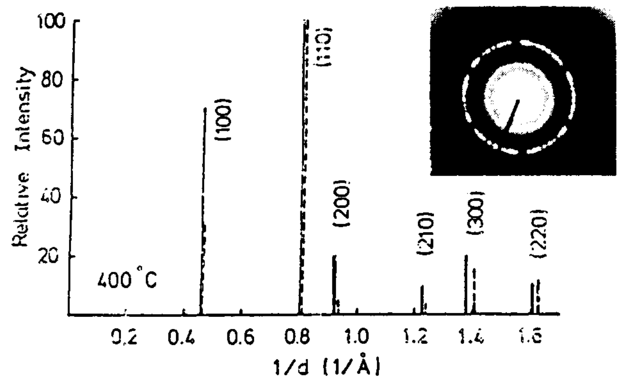

Figure 5. Reflection intensity versus 1/d of <001> oriented graphite.

In Fig. 6 are shown a TED pattern and a relation of the refletion intensity vs 1/d of polycrystalline pseudo-diamond(fcc) carbon. In the figure, calculated intensities (dashed lines), which were calculated by assuming a ZnS structure with a carbon atom occupation probability of 0.2 at 4c sites, agree well with the observed ones (solid lines). We often observe single crystal TED patterns of the pseudo-diamond (fcc) structure. Photo 2 shows a typical example of the TED pattern and the corresponding TEM image taken from a single crystal.

IV. Conclusions

By the inductance-type technique, the pseudo-polymer phase was formed at substrate temperatures from room to

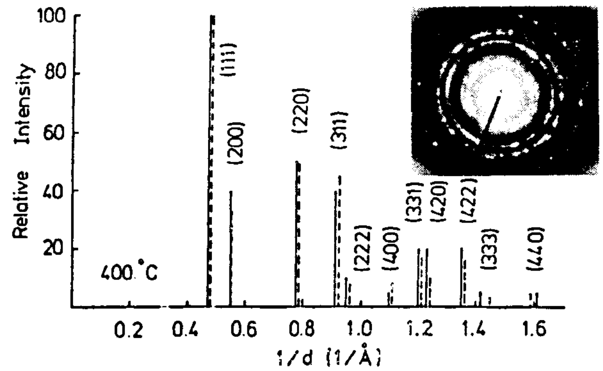

Figure 6. Reflection intensity versus 1/d of pseudo-diamond.

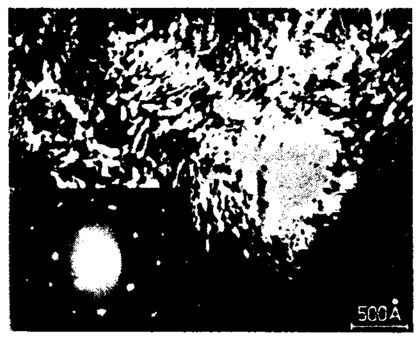

Photo 2. TEM and TED of single crystal fcc carbon.

200℃ and graphite phase was recognized at temperatures between 300 and 500℃. On the other hand, by the capacitance-type technique, randomly oriented polycrystalline graphite phase appeared between room temperature and 200℃, and then perfectly <001> oriented graphite phase and pseudo-diamond phase were recognized at temperatures from 300 to 450℃. The amorphous carbon structure is usually formed at any temperature range independent of the deposition techniques.

1)Y.Ichinose et al.; 16th Bienn. Conf.(1983,San Diego)
2)Y.Ichinose et al.; Int. Carbon Conf.(1984,Bordeaux)