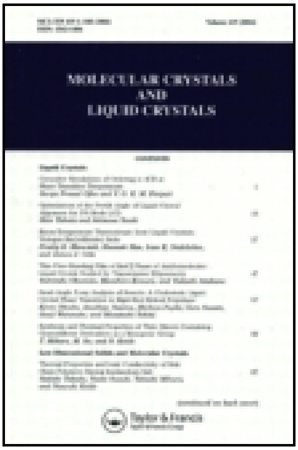

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Study of Fabrication of Organic-Inorganic Composite Circuit by Simultaneous Vacuum Deposition

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Study of Fabrication of Organic-Inorganic Composite Circuit by Simultaneous Vacuum Deposition

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Self-organization of an organic-inorganic composite circuit by simultaneous vacuum deposition of organic-inorganic materials was suggested by electrical conductivity along the film plane measured in situ during the deposition.

Keyword: Organic-inorganic composite; co-deposition; In situ measurement; electrical conductivity

INTRODUCTION

First, an organic-inorganic composite film preparation was tried by means of the simultaneous evaporation of various metals such as copper (Cu) and nickel (Ni) and organic molecules like phthalocyanine (Pc) [1,2]. As a result, it was found that the metallo-phthalocyanine complex (MPc) was synthesized in a vacuum process [1,2], and also that the aggregation of metal Pc and MPc was remarkably prevented. The metal cluster dispersed up to 1nm [3,4]. It was also pointed out that preventing Pc aggregation is an important factor to the complex formation of MPc in the vacuum process 3,4). On the other hand, by co-deposition of tetracyanobenzene which is raw materials of Pc and copper, copper phthalocyanine complex (CuPc) polymer was synthesized by Yudasaka5). And, Feifar et al had shown the formation of CuPc by co-deposition of Cu and Pc in vacuum6).

To search functional applications on such new organic-inorganic composite materials in the future, it is desirable to know the situation of a formation of nano-composite structure during the co-deposition process. To that end, in the present paper, two- or three-dimensional electrical connections of the composite were investigated by in situ measurement of electrical conductivity, which varies with film thickness . A composite of organic molecules and inorganic metal had been previously found to show high electrical conductivity in the sample of stearic acid or paraffin and several kinds of metal as Al 7).

EXPERIMENT

As inorganic components, Cu (purity 99.95 %) from Wako Junyaku Co., Ltd. and indium (In) from Kanto Chemicals Co., Ltd. were used. Pc reagent from Wako Junyaku Co., Ltd was used as the organic component without further purification. The degree of vacuum during the vapor deposition was 2×10^{-5}t orr, the deposition rate of Pc was 0.03nm/s (constant), and the deposition rate of Cu and In (V_{cu},V_{In}) was changed to 0.01, 0.02, 0.05, and 0.10nm/s. Substrate temperature was kept at 13 ℃ and the electrical resistivity of the sample was measured using a digital multimeter (R 6581, Advantest Co., Ltd.).

Sets of Pc and Cu or Pc and In were co-deposited respectively on the slideglass in vacuo from different evaporation sources, as shown in Fig.1(a). Before the co-deposition, the Au electrode was coated on the slideglass by the vacuum deposition method, as shown in Fig.1(b). The electrical conductivity σ(S / cm) along the plane of the sample was measured in situ during the codeposition.

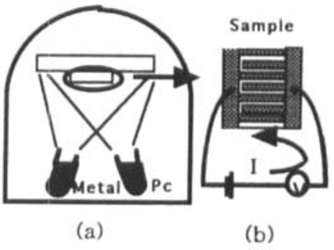

FIGURE 1 In situ measurement electrical conductivity.

RESULTS AND DISCUSSION

Fig.2 shows the experimental results at various Vcu. In the figure, three types of variation of electrical conductivity increase with the deposition thickness of Cu component were observed. The first type was observed in the case of Vcu=0.01nm/s, where Cu fraction is the smallest. The conductivity increases with two or three steps. The second type was observed in the case of Vcu=0.10nm/s, where Cu fraction is the largest. The conductivity increases with only one step. The type was observed in the case of Vcu=0.02nm/s, where Cu fraction is medium. Conductivity increases when mixing the former two types. Electrical conductivity of only Cu vapor deposition (O-Cu, Vcu=0.02nm/s) showed a similar and clear dependence on the Cu deposition thickness, as that of the sample at Vcu=0.01nm/s. When Cu deposition rate is slow, electrical conductivity of Cu × Pc changes similarly with that of O-Cu.

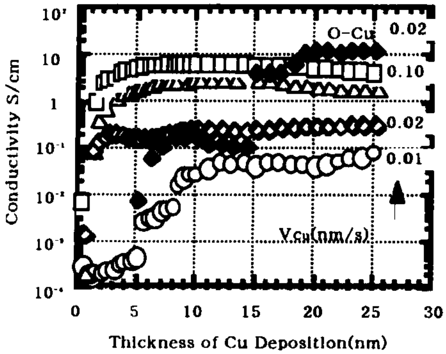

FIGURE 2 Electrical conductivity of Pc × Cu. Solid symbols show the O-Cu sample.

Next, a similar examination was tried on the co-deposition of In and Pc (In × Pc). In this case, large cohesion of metal was observed. Therefore, by replacing metal species, a change of electrical conductivity is expected. As shown in Fig.3, a different conductivity change was observed with thickness in the In component.

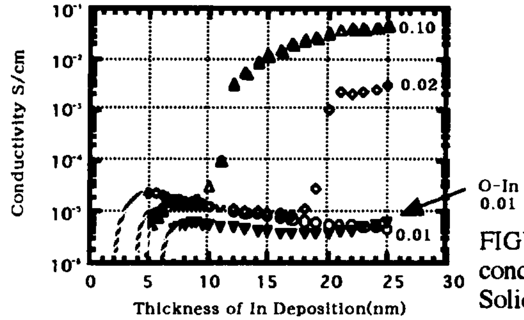

FIGURE 3 Electrical conductivity of Pc × In. Solid symbols show the O-In sample.

The conductivity of only the Indium vapor deposition(O-In) at V_{In}=0.01nm/s did not increase at all the range of In thickness. In the case of V_{In}=0.02~0.10 nm/s, the conductivity did not increase until 10nm In thickness. As V_{In} became faster, however, the conductivity began to increase. In the sample of V_{In}=0.01nm/s, conductivity did not show any increase in the measured region. This was different from the case of the sample Pc × Cu. This difference should be based on the difference in the aggregation state of both samples of Pc × Cu and Pc × In. The conductivity of Pc × In at $V_{In} \geqq 0.02$nm/s is larger than that of O-In.

To understand this phenomenon in detail, the direct observation of aggregation in the sample by means of transmission electron microscope (TEM) provides considerable information. Some examples are shown in Figs. 4 and 5.

Mean sizes of metal cluster and gap among clusters were estimated from TEM images. It was found that Cu cluster size was very small (2.09nm), and gap size was 4.69nm in the sample co-deposited under V_{Cu}=0.01nm/s and Cu deposition thickness (D_{Cu}) of 2nm. Further, in the sample deposited at V_{Cu} = 0.10nm/s and D_{Cu}=15nm, it was found that cluster size became the largest (4.43nm), whereas gap size became the narrowest (3.03nm).

On the other hand, TEM image of the Pc × In (shown in Fig.5) indicates that the sample deposited at V_{In}=0.10nm/s and D_{In}=15nm has a large cluster size of 47.16nm and that the aggregation occurs considerably. A large gap of 6.29nm was observed.

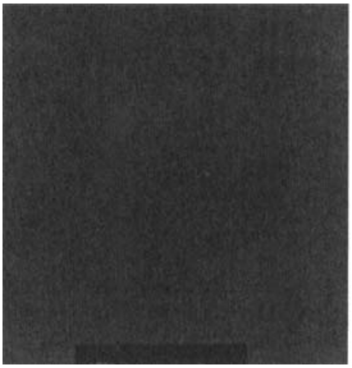

FIG.4 TEM image of Pc × Cu. Vcu=0.10nm/s. DCu is 15nm.

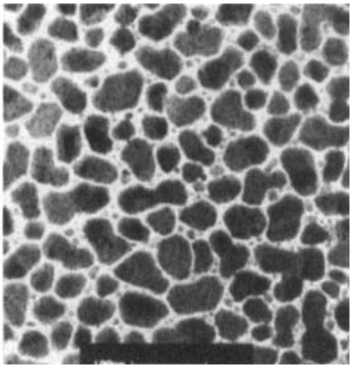

FIG.5 TEM image of Pc × In. VIn=0.10nm/s. DIn is 15nm.

From the structural analysis of each composite film, the growth of electrical connection of metal clusters during vapor deposition was suggested. Here we will show the schematic illustration of the structural growth of the sample Cu × Pc deposited at Vcu=0.01nm/s (see the insert in Fig.6).

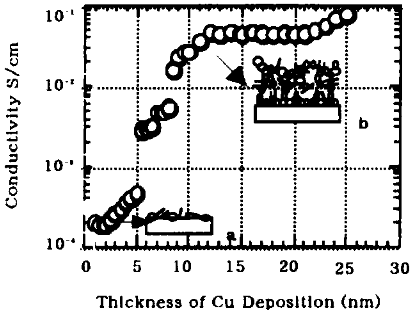

FIGURE 6 Schematic illustration of Vcu=0.01nm/s of the Cu × Pc.

This sample has the smallest Cu fraction. In the figure, (a) shows that Pc molecules and Cu clusters are dispersed two-dimensionally on the substrate. (b) shows that the Cu cluster begins to form a three-dimensional electrical connection network. The space of the model may be filled with Pc.

The structure of the In × Pc deposited at VIn=0.10nm/s, on the other hand, is illustrated as shown in Fig.7. In particles connect each other at higher density; however, the co-deposition of Pc seems to have an influence to prevent the growth of large In particles. From the result of large electrical conductivity in the In × Pc sample deposited at VIn≧0.02nm/s (Fig.3), the Pc co-deposition seems to make a similar structure of In × Pc to that of Cu × Pc, as shown in Fig.6.

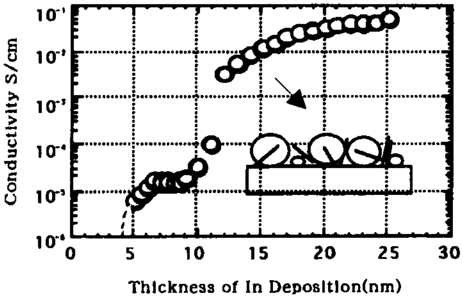

FIGURE 7 Schematic illustration of VIn=0.10nm/s of the In × Pc.

Acknowledgments

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