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Electronic Transport Properties of C_{60} Derivative Self-Assembly Monolayer on Au Ultrathin Film

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About four decades ago Little and Ginzburg proposed low dimensional excitonic room temperature superconductors. We have noticed that a Self-Assembly Monolayer by C_{60} derivatives (C_{60}-SAM) formed on ultrathin metal films may become the substance model proposed by them. The C_{60} derivative used was C_{60}-O-C8SH and preferentially absorbed on Au surfaces. When MgO(100) substrates were annealed at 900℃, the surfaces had step-terrace structures with 1–2nm height of bunching steps. After deposition of Au ultrathin films on the MgO by RF magnetron sputtering the substrates were soaked in a 0.01mM benzene solution of C_{60} derivatives for 20h at room temperature. AFM images revealed that the C_{60}-SAM aligned one-dimensionally along the edges of steps. The temperature dependences of resistance were measured by a four probe technique. Some of the samples showed anomalous decreases of resistance in the temperature range of 250 – 150K. The mechanisms of the resistively anomaly have been discussed.

Key words: C_{60}, Self-Assembly Monolayer, Ultrathin Au Film, High Temperature Superconductivity

1. INTRODUCTION

As well known Little[1] and Ginzburg[2] proposed the room temperature superconductivity by an excitonic mechanism. They discussed the possibility of the room temperature superconductivity by the exciton in the 1-dimensional system and the 2-dimensional system, respectively. Then the expected Tc is above room temperature.

In the models the exciton parts (the side chain) which are adjacent to electron conducting parts (the main chain) must have enough high energy and interactions with electrons. The candidate of the main chain for the 2-dimensional system is a metal. Since the shielding length of the exciton in metals may be in the order of nm, the metal layer must be ultrathin and continuous.

As the side chain π electronic molecules may be available from the point of view of excitonic energy. Especially we have noticed at a C_{60} molecule because of its physical and chemical stability or easiness for handling. Shi *et al*[3]. reported the preparation of highly closed packing alignments of the C_{60} derivatives (C_{60}-O-C_6SH) self-assembled monolayer (C_{60}-SAM) on Au (111) / mica substrates. The monomolecular layer of the C_{60} derivative may be adopted for the side chain.

In this work the used C_{60} derivative was C_{60}-O-C_8SH. The details of the derivative were appeared in elesewhere[4]. Au ultrathin films were prepared on MgO substrates which had atomically flat surfaces. When the C_{60}-SAM's are synthesized on Au ultrathin films, we expect that the substance system becomes the model of a room temperature superconductor.

The surface morphology and structure of the surfaces are evaluated and the temperature dependences of resistance of the specimen films were measured.

2. EXPERIMENTAL

Au thin films were prepared on MgO substrates which were annealed in a gold furnace. The two MgO (100) substrates were faced to each other surface and piled on black Nb doped – $SrTiO_3$. The annealing temperature was increased with the speed of 450 ℃/h and was kept at 900 ℃ for 12 hour. The temperature was cooled down with the speed of 450 ℃/h and the substrates were taken out at room temperature.

As the electrodes for resistance measurements and the area of ultrathin metallic films Au films were prepared simultaneously on the MgO substrate by RF magnetron sputtering through a metal mask. Sputtered Au flux passed around behind the holes of the mask. The diameter of the hole was determined by chemical etching time and the distance between the holes was about 190 μ m. By adjusting the distance between the mask and the substrates the diameter of deposited Au electrodes was changed.

The used target was a Au plate with a diameter of 80mm. The conditions of sputtering were: substrate heating temperature of 400 ℃, Ar gas pressure of 1.2

Pa, sputtering power of 100 W, and sputtering time of 10 min.

In the SAM process schematically shown in Fig. 1, the Au/MgO substrates were soaked in benzene solution of 0.01 mM C_{60} derivatives for 20 hour at room temperature[4]. After the soaking non-adsorbed C_{60} derivatives were washed out by benzene and the specimen was dried by dry N_2 gas.

The surface morphology of the specimen films was observed by an Atomic Force Microscopy (AFM) (Seiko Instruments Inc.). The electrical conductivity was measured by a four probe technique.

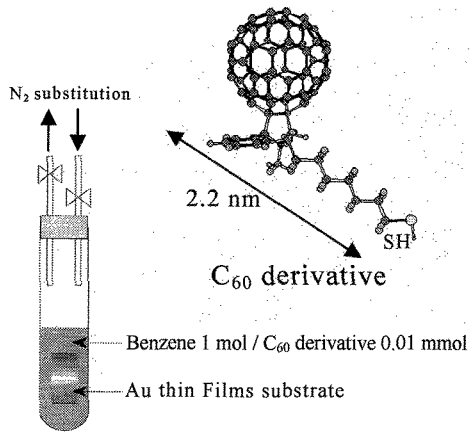

Fig.1 Schematic view of C_{60}−SAM process and the C_{60} derivative.

3. RESULTS AND DISCUSSION

The typical cross section of the prepared specimen is shown schematically in Fig. 2. The diameter of the Au electrodes was about 170 μ m. The width of the valley in which ultrathin Au films were deposited was less than 20 μ m length. The C_{60}-SAM was formed all over the surface.

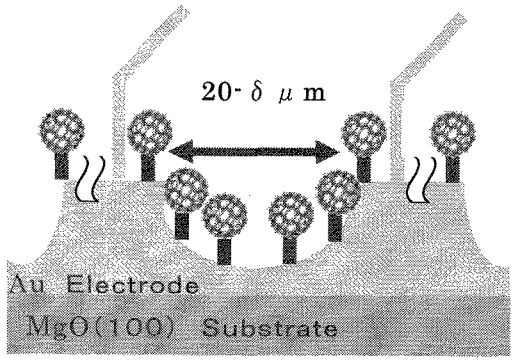

Fig.2 Schematic view of a cross section of the specimen.

The AFM image of the C_{60}-SAM formed on ultrathin Au films is shown in Fig. 3. The enlarged image is shown in the inset. The line profile is also shown in the attached figure. It was found that C_{60}-SAM's aligned one-dimensionally along the edges of steps of MgO surfaces. The bright lines in the figure revealed that the height of the accumulated materials was 1.0-1.5nm and the width of the SAM region was narrow, a few tens nm. Since the length of the C_{60} derivative is 2.2 nm, C_{60}-SAM's may be accumulated in canting.

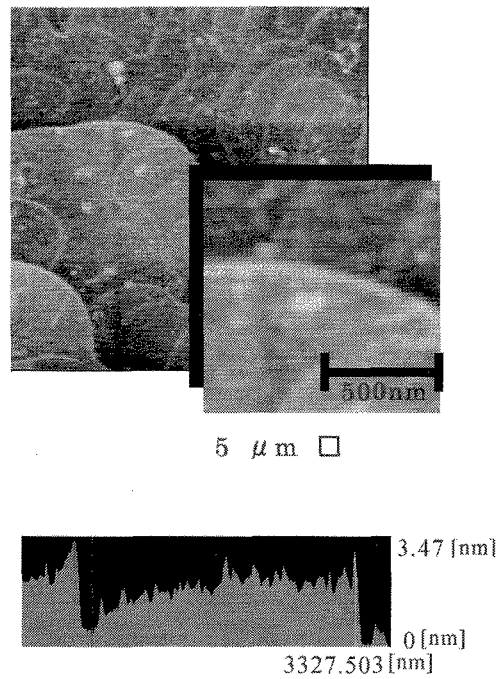

Fig.3 The AFM image and the line profile of C_{60} - SAM / Au // MgO.

The temperature dependence of resistance was measured. In normal metal films the resistance decreases linearly as decreasing temperature. Several specimens showed, however, anomalous decreases of resistance. Figure 4 shows such the typical temperature dependence of resistance which was 凸-shaped and slightly deviated from the linear line.

The differential coefficient of resistance vs. temperature is shown in Fig. 5. The value of the differential coefficient increases rapidly in the temperature of about 150K. It means that resistance decreased rapidly in the temperature range by some other mechanism rather than usual lattice vibrations.

This type of resistively anomaly was observed only in the specimen with ultrathin Au films. The thickness of the Au film varied in the film plane because of a large distribution of Au flux sputtered from the target. The temperature dependence of resistance was measured at three different points in one specimen for comparing and discussing the influence of the thickness of the Au films. The results are shown in Fig. 6. In the two points where Au film was comparatively thick, resistance revealed the normal metallic behavior. However, the specimen of ultrathin Au films showed remarkable anomalous decreases of resistance in the temperature range of 150-250K.

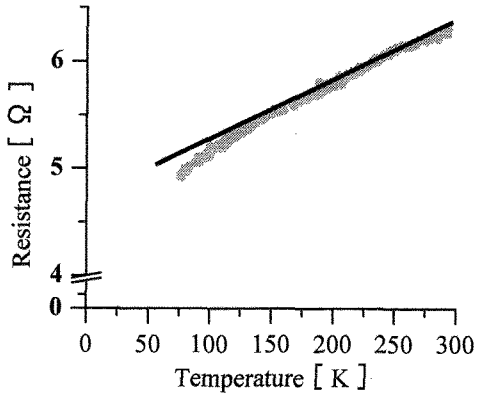

Fig.4 The typical temperature dependence of resistance of C_{60} - SAM / Au // MgO.

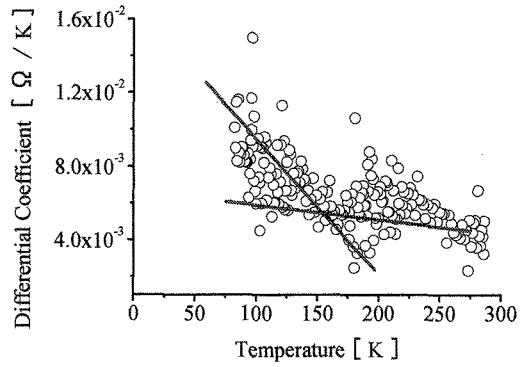

Fig.5 The absolute value of differential coefficient of resistance vs. temperature in the C_{60} - SAM specimen of Fig.4.

The anomalous temperature dependence of resistance was fitted in the two temperature regions with the linear lines. If we assume that only the limited region of the specimen changes into a zero-resistance state at Tc, the linear lines would have a step as shown in Fig. 7. Then the other regions of the specimen are in normal metallic state.

We think that the observed phenomenon was caused by the influence of excitonic interactions between free electrons in the metal and electric dipoles excited in the molecules. Since the shielding length in metals was so small, the order of nm, the anomalous effect may be suppressed in the region of thick Au films,.

The transition width of resistance observed was very broad. This is interpreted as the result of large fluctuations which are usually appeared in a low dimensional system.

4. CONCLUSION

The interface of ultrathin metallic films/organic molecules was proposed as a novel substance model of an excitonic superconductor.

The Au ultrathin films were deposited by RF magnetron sputtering. The morphology and structure of the specimen surfaces were observed. The C_{60}-SAM

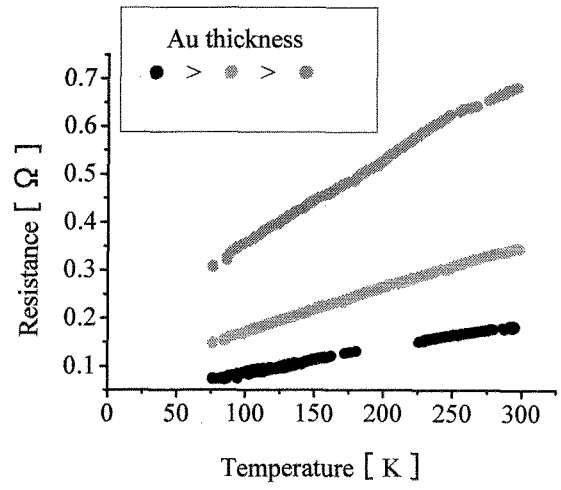

Fig.6 Temperature dependences of resistance at three different points in one specimen where the Au film thickness was different.

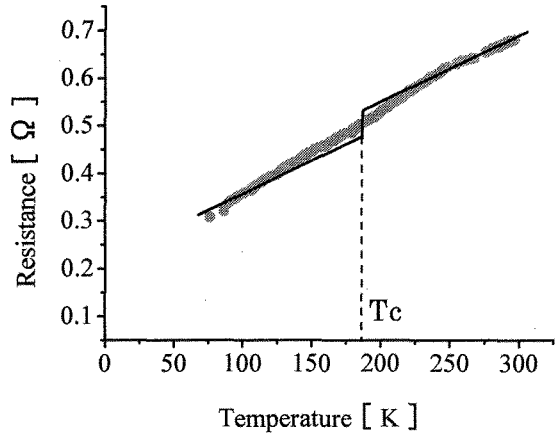

Fig.7 The resistively anomaly and temperature dependence of resistance expected in the C_{60} - SAM / Au accompanying with a zero resistance region.

adsorbed on the Au films was accumulated in 1-dimensional alignment along the edges of steps of MgO(100) substrates. The some specimen showed the anomalous decreases of resistance which were observed in the temperature range of 150K-250K. This may be caused by the change of a conducting mechanism in the interface of C60 derivatives/ultrathin Au through an excitonic mechanism. The detailed properties of such specimen will be investigated. Also the sample preparation conditions have been considered to obtain the better reproducibility for these anomalous phenomena.

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