Nano-Structured C_{60}-SAM Formed on Ultrathin Au Films/MgO Single Crystal

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ABSTRACT

Exotic electric conducting properties have been expected in organic molecules/metals interfaces with low-dimensional nano-structures. A self-assembly monolayer of a C_{60} derivative, C_{60}-O-C_8SH, (C_{60}-SAM) was synthesized on ultrathin Au films which were deposited on MgO (100) single crystal substrates. Since the surfaces of annealed MgO were atomically flat and revealed step-terrace structures, the ultrathin Au films were deposited along the edges of the steps with the length of a few micro-meter. As the result of the characteristic nano-structure of the Au films, the C_{60}-SAM adsorbed on them showed also one-dimensional alignments with the width of few tens nm. The surface morphology of the C_{60}-SAM/Au was observed and analyzed by AFM. In particular samples the resistivity deviated from a normal linear dependence on temperature and revealed an anomalous decrease in the temperature range of 150 - 250K.

Keywords: C_{60}, self-assembly-monolayer, nano-structure, resistivity anomaly

1 INTRODUCTION

Exotic electric conducting properties have been expected in organic molecules/metals interfaces with low-dimensional nano-structures. It is well known that Little[1] or 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 T_c is above room temperature.

As shown in Fig. 1 the 2-dimensional model is consisted with the exciton parts (the side plane) which are adjacent to electron conducting layer (the main conducting plane). The side plane must have enough high energy of elementary excitation and interactions with free electrons in the conducting plane.

The candidate of the conducting layer for the 2-dimensional system is a metal thin film. Since the shielding length of the exciton in metals is in the order of nm, the metal layer must be continuous and/or ultrathin.

As the side plane π-electronic molecules layers may be available because of the high excitonic energy in the order of eV. In this work we have noticed a C_{60} derivative monolayer as the side plane because of its physical and chemical stability or easiness for handling. Recently Shi *et al*[3]. reported the preparation of highly closed packing alignments of the C_{60} derivatives self-assembled monolayer (C_{60}-SAM) on Au (111) / mica substrates. They used the C_{60} derivative (C_{60}-O-C_6SH) with alkanethiol at the end of long alkyl chain. Such the monomolecular layer of the C_{60} derivative may be adopted for the side chain.

We prepared a similar C_{60} derivative. 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 the excitonic superconductor.

The detailed experimental conditions are explained. The surface structure of the specimen films are evaluated and the observed temperature dependences of resistance are discussed.

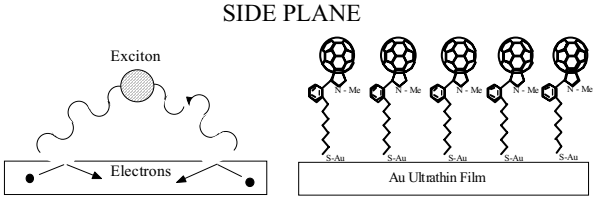


Figure 1: The schematic model of a 2-dimensional excitonic superconductor and the materials system proposed in this work.

2 EXPERIMENTAL

As the substrates MgO (100) single crystals were annealed in a gold furnace. The two MgO (100) substrates were faced to each other surface and piled on a Nb-STO crystal which effectively absorbed infra-red rays.[4] The annealing temperature was increased with the speed of 450 K/h and was kept at 1173-1273 K for 12 hour. The temperature was cooled down with the speed of 450 K/h and the specimen was taken out at room temperature.

Au films were prepared simultaneously on the MgO substrate by RF magnetron sputtering through a metal mask in order to obtain the both the electrodes for resistance measurements and the area of ultrathin metallic films.

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 190μm. By adjusting the distance between the mask and the substrates the diameter of the Au electrodes was changed to obtain one of typically about 170μm.

The used target was a Au plate with a diameter of 80mm. The conditions of sputtering were: distance between target and substrates of 10 cm, substrate heater temperature of 673 K, Ar gas pressure of 1.2 Pa, sputtering power of 100 W, and sputtering time of 10 min.

The C_{60} derivative (C_{60}-O-C_8SH) with a long alkyl chain was synthesized by following the similar method previously reported[3]. The molecule was schematically shown in Fig. 2. The synthesized powder was purified by the HPLC with Buckyprep column (Nacalai Tesque Co.) and toluene, and characterized by FAB-MS and H-NMR spectroscopy. The length of the C_{60} derivative is calculated to be 2.2 nm by a space-filling model.

In the SAM process the C_{60} derivatives strongly adsorb on Au with alkanethiol and form monomolecular layer in highly dense structures. The SAM process is illustrated in Fig. 2. The Au/MgO substrates were soaked in benzene solution of 0.01 mM C_{60} derivatives. The soaking cell was filled with N_2 gas. After the soak non-adsorbed C_{60} derivatives were washed out by benzene and the specimen was dried by dry N_2 gas.

Figure 2: Schematic equipment of the SAM process and the used C_{60} derivative (C_{60}-O-C_8SH). The soaking cell was filled with N_2 gas. The soak was done at room temperature for 20 hr.

The depth profile of XPS C_{1s} peak intensity indicated the existence of C_{60} derivatives monomolecular layer on Au films. The covering ratio of the C_{60} derivatives was evaluated by comparing the intensity of the XPS C_{1s} peak of SAM with that of evaporated C_{60} films. The value of the covering ratio increased as increasing the soaking time until about 10 hr and almost saturated for 15 hr at room temperature.[5] So the specimen were soaked typically for 20 hr in this work.

The surface morphology of the specimen films was observed by an Atomic Force Microscopy (AFM) (Seiko Instruments Inc.). The resistance of the specimen was measured by a four probe technique in the temperature range from 300 K to 77 K.

3 RESULTS AND DISCUSSION

The typical cross section of the prepared specimen is shown schematically in Fig. 3. The diameter of the Au electrodes was about 170μm. The width of the valley in which ultrathin Au films were deposited was less than 20μm length. The C_{60}-SAM was formed all over the specimen surface.

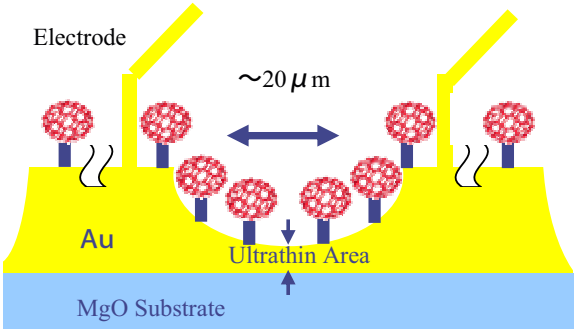
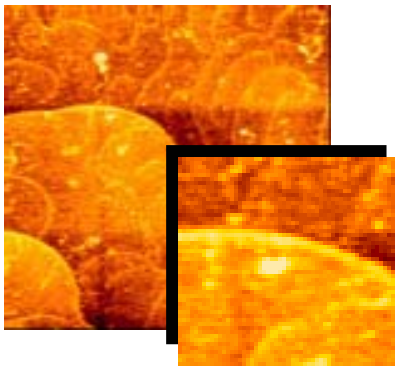


Figure 3: Schematic cross section of the SAM specimen and the Au configuration of electrodes.

The AFM image of the C_{60}-SAM formed on ultrathin Au films is shown in Fig. 4. 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 edge of the steps of the MgO. The bright lines in the figure revealed that the height of the accumulated substances 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.

The temperature dependence of the resistance was measured. In normal Au films resistance decreased linearly as decreasing temperature. Several specimens showed anomalous decreases of the resistance. Figure 5 shows such the typical temperature dependence of resistance. It revealed a 凸-shape and slightly deviated from the linear dependence in the temperature range below 150 K. The value of the differentiation coefficient of resistance vs. temperature increases rapidly from 5.0×10^{-3} to 8.0×10^{-3} ohm/K at about 150K. It means that resistance decreased rapidly in the temperature range by some other mechanism rather than usual lattice vibrations.



(a) The AFM image of surface morphology of the SAM specimen of 5μm square. The inset is the enlarged image of 1 μm square.

(b) The line profile of AFM in the length of 5μm. The maximum height of the rectangular is 3.47 nm.

Figure 4: AFM image and line profile of the SAM formed on ultrathin Au films/MgO (100) single crystal.

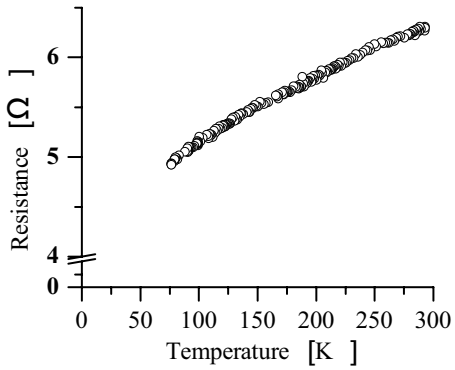


Figure 5: The typical temperature dependence of resistance of the SAM specimen.

This type of resistivity anomaly was observed only in the specimen with ultrathin Au films. As the evidence of the effect of Au film thickness the temperature dependences of the resistance were measured at three different points in one specimen for comparing and discussing the effect of the thickness of the Au films. The results is shown in Fig. 6.

In the two points where Au film was comparatively thick, resistance revealed the normal metallic temperature dependence. However, the part of ultrathin Au film showed remarkable anomalous decreases of resistance in the temperature range of 150-250K.

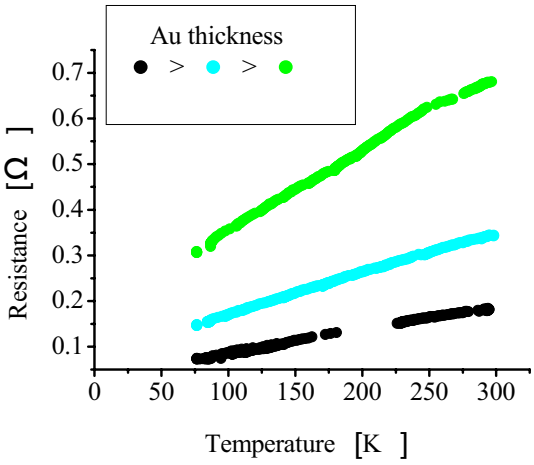


Figure 6: Temperature dependences at three different parts of the same SAM specimen. The upper line corresponds the thinner Au film.

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 the peculiar temperature, the linear line bends accompanying with a drop of resistance. Then the other regions of the specimen were normal metallic state and give finite resistance.

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. The anomalous effect may be suppressed in the region of thick Au films, since the shielding length in metals was so small, nm order.

The transition width of resistance was very broad. This may be interpreted as the result of large fluctuations which usually take place in a low dimensional system.

4 SUMMARY

The characteristic interface of ultrathin Au films/ C_{60} derivative monomolecular layer was proposed as the novel substance model for an excitonic superconductor.

The Au ultrathin films were deposited by RF magnetron sputtering. The C_{60}-SAM adsorbed on the Au films was accumulated in 1-dimensional alignment along the edges of the steps of MgO(100) substrates. The surface morphology and structure of the specimen were observed. The some specimen showed the anomalous decreases of resistance

which were observed in the temperature range of 150K-250K. These exotic behaviors may be caused by the change of conductivity in the interface of ultrathin Au/C60 derivatives through an excitonic mechanism.

The detailed measurement and analyses of resistance in the micro-scaled area of the specimens are now proceeded and the future subject.

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