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Nano-Structured Alignment of C_{60}

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Sapphire (0001) and (1$\bar{1}$02) substrates were annealed at 1000°C for 12 h in air to obtain flat surfaces with a step-terrace structure. Au films were deposited on the substrates using the molecular beam epitaxy (MBE) method, at various substrate temperatures. The surface morphology of the films was observed by means of atomic force microscopy (AFM). A quasi one-dimensional alignment of Au particles was partially prepared along the steps at the sapphire (0001) substrate temperature of 620°C. On the other hand, an atomically flat Au thin film was obtained at the low substrate temperature of 300°C (at sapphire (1$\bar{1}$02)) and 130°C (at sapphire (0001)). A C_{60} monolayer was obtained by re-evaporating the C_{60} molecules deposited on the Au films, which was confirmed by X-ray photoelectron spectroscopy (XPS).
Key words: C_{60} monolayer, nanostructure, step, terrace, diffusion barrier, atomic force microscopy (AFM)

1. INTRODUCTION

Recently, the fabrication of electronic devices has reached the nanoscale level with the continued increase in the density of integration. Therefore, the fabrication processes of devices are becoming increasingly complicated and costly. The aim of this study is to fabricate a nanoscale structure with functional molecules, in particular, a monolayer of C_{60} molecules was aligned one- and/or two-dimensionally by a re-evaporation method. In this method, an important aspect is that the binding between C_{60} and metals is stronger than that among the C_{60} molecules. After the growth of C_{60} / Au and annealing, only those C_{60} molecules directly adsorbed onto metals remained, whereas the molecules bound with a weak Van der Waals interaction were re-evaporated.

Then the alignment of metals is a particularly important process for obtaining nano-structured C_{60} films. We have taken note of the surface structure of oxide single crystal substrates. A simple process has been reported for obtaining atomically flat surfaces with a step-terrace structure.[1,2] On such substrates, Au films were deposited by molecular beam epitaxy (MBE) while changing the substrate temperature. The surface morphology of the obtained films was observed and discussed with respect to the synthesis of nano-structured C_{60} monolayers.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows the process proposed for the fabrication of C_{60} low-dimensional structures, particularly the one-dimensional (1D) structure. (a) The substrates with step-terrace structures are prepared. (b) 1D Au alignments are formed along the steps of the substrates. It is expected that the steps function as a potential barrier for the migration of Au atoms and Au particles aligned along the steps. Therefore, a high substrate temperature and/or a low Au flux rate are a desirable condition. For the two-dimensional (2D) alignment of Au particles, a low substrate temperature is

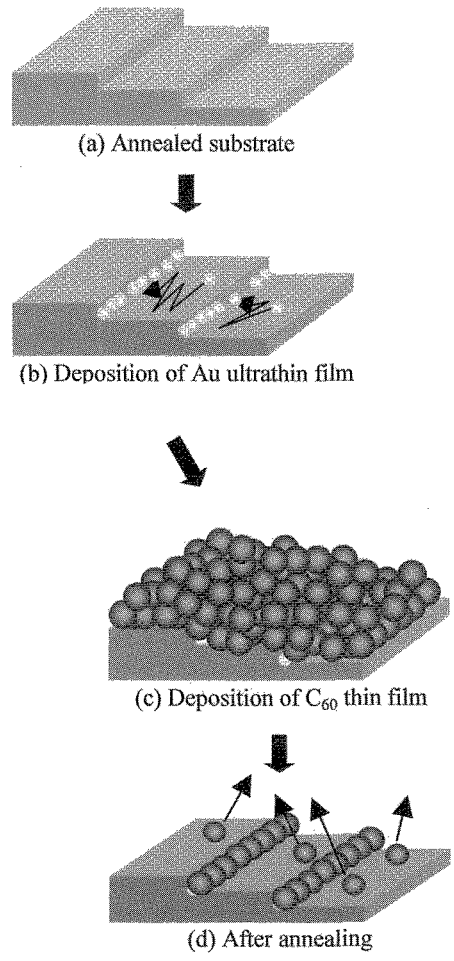


Fig. 1. Schematic images of proposed process for the fabrication of C_{60} low-dimensional structures on Au layers. (a) Step-terrace structure of single crystal surface, (b) one-dimensional alignment of Au, (c) as-grown C_{60} film and (d) one-dimensional alignment of C_{60}.

possibly an appropriate condition. (c) C_{60} molecules are deposited on the substrates. (d) Annealing is carried out *in situ* to re-evaporate only those C_{60} molecules bound with weak Van der Waals interactions.[3)]

Table I. Conditions of film growth.

	K-Cell temperature(°C)	Substrates temperature(°C)	Deposition time (min)	Annealing after deposition	
Au	1200-1300	130-630	1.5-40	130-630°C	30 min
C_{60}	~310	190	5-10	~350°C	30 min

Films were grown using an MBE system which was evacuated by a diffusion pump and a turbomolecular pump. The background pressure was approximately 1×10^{-8} Torr.

After the Al_2O_3 substrates are cleaned ultrasonically in acetone and particular Al_2O_3 $(1\bar{1}02)$ substrates add to HF treatment, they are annealed at 1000°C for 12 h in air. The annealed substrates are pre-baked at 400°C for 30 min in vacuum, prior to the deposition. The growth temperatures of the substrates are measured using an optical pyrometer. Au with 99.99% purity and C_{60} powder with 99.95% purity are evaporated from pyrolytic boron nitride (PBN) crucibles in Knudsen cells. Table I shows the details of conditions for film growth. Au deposition is usually completed after the appearance of additional spots and/or rings of Au in the reflection high-energy electron diffraction (RHEED) pattern of the substrate. During the deposition, the temperature of the C_{60} K-Cell is controlled in order to maintain a constant flux rate using a crystal thickness monitor.

The surfaces of the films were observed *in situ* by RHEED during deposition and annealing. After the air exposure of the samples, the surface morphology was measured by atomic force microscopy (AFM) (Seiko Instruments Inc. SII: SPI3800) and the chemical binding condition of C_{60} was measured by X-ray photoelectron spectroscopy (XPS) (SHIMADZU Co. : ESCA-850, X-ray: MgKα). The XPS peaks were detected every 6 s during etching by Ar ions accelerated at 2 kV. The sample size was approximately 3 mm^2. Vertical differential charging was calibrated by the Au $4f_{5/2}$ peak.

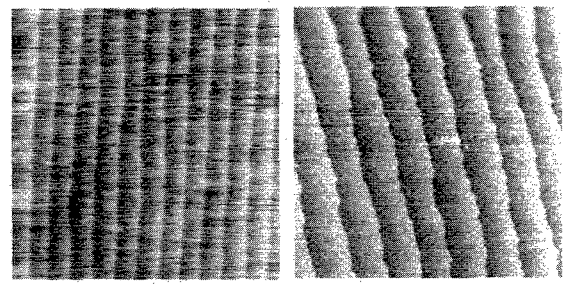
Resistivity was measured by the four-point probe method. Comb-type Au electrodes were prepared on the substrate prior to the film deposition.

3. RESULTS AND DISCUSSION

3.1 Surfaces of substrates

Figure 2 (a) and (b) show AFM images of a sapphire substrate annealed at 1000°C for 12 h. The sapphire (0001) surface (Fig.2 (a)) shows uniform parallel steps and atomically flat terraces with 0.21 nm step height and approximately 80 nm terrace width. The sapphire $(1\bar{1}02)$ surface (Fig.2 (b)) shows jagged step edge and atomically flat terraces with approximately 0.35 nm step height and approximately 100 nm terrace width.

Uniform parallel steps are suitable for electrical conduction measurements of the Au particles one-dimensionally aligned along the steps. The step height is available for the steps function as a potential barrier for the migration of Au atoms.



(a) (b)

Fig. 2. AFM images (1000 nm^2) of (a) α-Al_2O_3 (0001) and (b) α-Al_2O_3 $(1\bar{1}02)$ substrate

3.2 One-dimensional structure

Figure 3 shows the AFM images of Au particles evaporated on the annealed sapphire (0001) substrates under the substrate temperature conditions (*T*s) of (a) 350°C, (b) 500°C and (c) 620°C. The Au flux was fixed at 1.64 mTorr, which was derived from the temperature dependence of the equilibrium vapor pressure. The Au particles with diameters of approximately 10 nm were distributed without alignment at the *T*s of (a) 350°C and (b) 500°C. At the *T*s of (c) 620°C, particles had diameters of approximately 20 nm and were aligned partially along the lower and/or higher sides of the substrate steps. Fig. 3 (d) shows the AFM image of Au particles deposited at the *T*s of 620°C under the Au flux of 0.820 mTorr. In this case, comparatively small Au particles with diameters of approximately 13 nm tended to align around the steps. From the comparison of the results in Figs. 3 (c) with those in 3 (d), it is confirmed that the diameter of the Au particles became smaller and the probability of the adherence of the Au particles at the steps became higher upon decreasing the flux rate.

By decreasing the flux rate and/or increasing the substrate temperature, the migration length of the deposited atoms increases. Therefore, the probability of the collision of atoms on the terraces was decreased, and then the deposited Au atoms reached the substrate steps and nucleated there. When atoms collide with other atoms on a terrace and grow beyond the critical radius of the nucleus, the collided particles do not reach the steps due to the higher potential barrier for migration, and thus they could form nucleation sites on the terrace.

As shown in Fig. 3 (d), the 1D nanostructure of Au particles appeared partially along the steps under the condition of *T*s =620°C and flux rate of 0.820 mTorr, under which condition the atoms can gain the migration energy required to reach the steps.

The Au particles become spherical as a general tendency because of the large difference in surface energy between Au and the substrate.[4)] It is considered that comparatively small Au particles are more suitable than large particles for 1D alignment through connecting with each other along the steps.

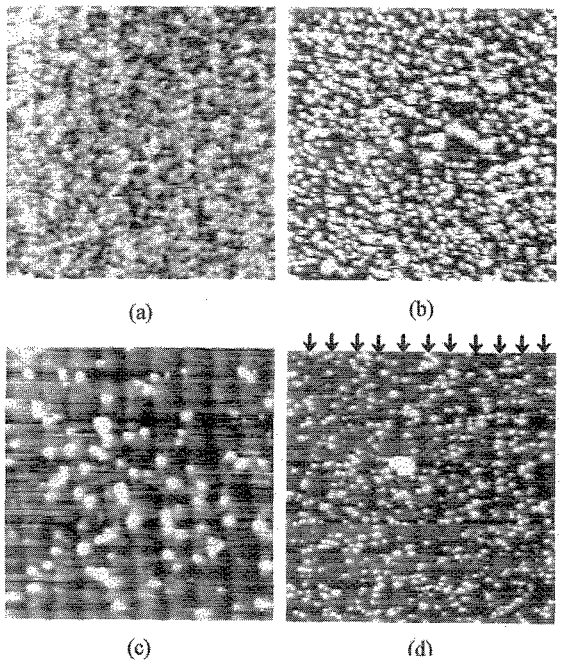


Fig. 3. AFM images (1000 nm^2) of Au particles deposited on α-Al_2O_3 (0001) substrate at different substrate temperatures of (a) 350°C, (b) 500°C ,(c) and (d) 620°C. Au flux rates for (a) – (c) were 1.64 mTorr and that for (d) was 0.820 mTorr.

3.3 Two-dimensional structure

Figure 4 shows the RHEED patterns of (a) the annealed surface of sapphire (0001) substrates, and (b) the Au thin film evaporated under the conditions of *T*s =130°C and the Au flux rate of 0.82 mTorr. The electron beam was incident from the [1$\bar{1}$00] direction perpendicular to the step lines. Fig.5 shows the RHEED patterns of (a) the annealed surface of sapphire (1$\bar{1}$02) substrates, and (b) the Au thin film evaporated under the conditions of *T*s =300°C and the Au flux rate of 0.82 mTorr. The electron beam was incident from the [1120] direction parallel to the step lines. After the deposition of Au, the characteristic pattern on the substrate disappeared and faint diffraction rings from Au were observed, indicating the growth of polycrystalline Au films.

Figure 4 (c) and Fig.5 (c) show AFM images of the Au film. The images are similar to that of the substrate, which indicate atomically flat Au thin films. This planar structured Au film was applied in the synthesis of a 2D structured C_{60} monolayer. The specimen was prepared by a process involving the deposition of C_{60} films on the 2D Au film and successive re-evaporation at 350°C.

Figure 6 shows an XPS spectrum of a C_{60} thin film after 6 s etching. This specimen was prepared on an Au thin film by the re-evaporation method. It is known that a monolayer of C_{60} on Au has a metallic property because of the charge transfer from Au to C_{60} and the XPS C1s peak with the tail extended to the higher binding energy side.[5,6]

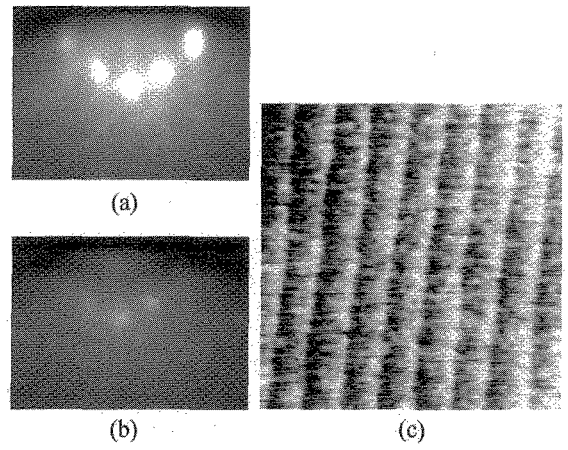


Fig. 4. RHEED patterns of (a) the annealed surface of α-Al_2O_3 (0001) and (b) deposited Au on Al_2O_3 substrate. Electron beam was incident from the [1$\bar{1}$00] direction. (c) AFM images (1000 nm^2) of deposited Au on Al_2O_3 at the substrate temperature of 130°C and flux rate of 0.820 mTorr.

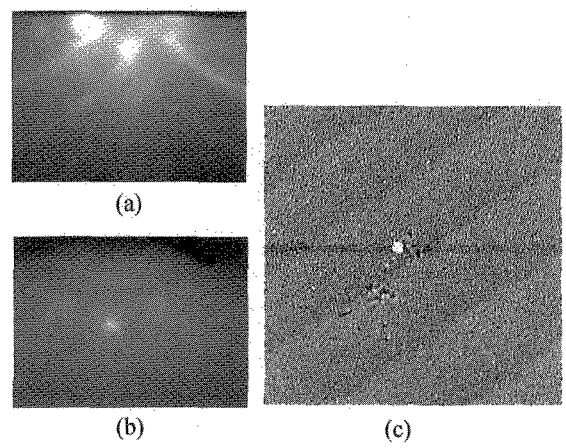


Fig. 5. RHEED patterns of (a) the annealed surface of α-Al_2O_3 (1$\bar{1}$02) and (b) deposited Au on Al_2O_3 substrate. Electron beam was incident from the [1120] direction. (c) AFM images (1000 nm^2) of deposited Au on Al_2O_3 at the substrate temperature of 300°C and flux rate of 0.820 mTorr.

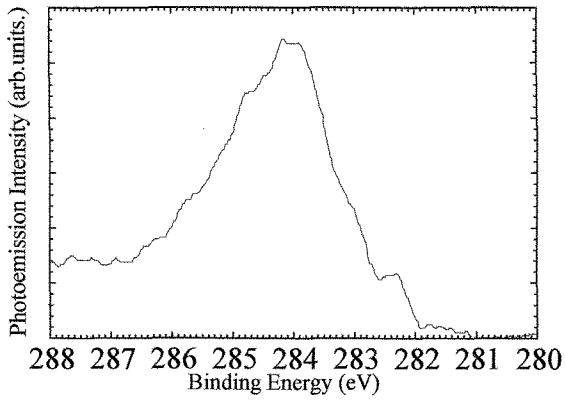


Fig. 6. XPS spectra of C1s peak of C_{60}/Au//Al_2O_3 (0001).

The observed asymmetric peak of the C_{60} film was consistent with the result for the C_{60} monolayer. Thus, it is apparent that the re-evaporation method is useful for the preparation of C_{60} monolayer on Au films.

The resistivity of the Au thin film was too high, namely, above 1 kΩ·cm, to be measured using our measurement system. However, it is expected that the electric conductivity of C_{60} monolayer can be measured and investigated in C_{60} films deposited on such a highly resistive Au film.

4. CONCLUSION

The 1D alignment of Au particles could be achieved on annealed α-Al_2O_3 (0001) substrates by increasing the substrate temperature and decreasing the flux rate because the steps function well as a potential barrier for the migration of Au atoms. The nanostructured 1D alignment of Au particles appeared partially along the steps under the condition of *Ts* =620°C and flux rate of 0.820 mTorr.

Atomically flat 2D Au thin films were deposited at *Ts* =130°C (α-Al_2O_3 (0001) substrates) and *Ts* =300°C (α-Al_2O_3 (1$\bar{1}$02) substrates) and the Au flux rate of 0.82 mTorr. After the C_{60} deposition on the Au thin film//Al_2O_3 (0001), the re-evaporation of C_{60} was carried out by annealing at 350°C. It was confirmed on the basis of XPS analysis that C_{60} monolayers can be synthesized on Au thin films by the re-evaporation method.

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