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SPATIALLY EXTENDED POLYMERIZATION OF C_{60} CLUSTERS INDUCED BY LOCALIZED CURRENT INJECTION FROM SCANNING TUNNELING MICROSCOPE TIPS

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The injection of tunneling electrons from tips of scanning tunneling microscopes (STM) to crystalline C_{60} films induces a change in STM images indicative of polymerization of the clusters, the efficiency of which is strongly affected by the internal strain in the film [Y. Nakamura et al., Appl. Phys. Lett., **77** *2834 (2000)]. The tip-induced polymerization effect in films deposited on Si substrates spreads spatially over ~10 nm from the electron injection point. However, the extent of the spread is reduced in films grown on graphite substrates presumably due to a difference in the intercluster spacing.*

Keywords: fullerenes; scanning tunneling microscopy; polymerization; electronic excitation; electron beam resist

INTRODUCTION

The polymerization of C_{60} (fullerene) clusters induced by light illumination is one of the many curious features of this material. This photo polymerization has been studied intensively because not only of the scientific interest but also of technological concerns on the use of fullerenes as a material of resistive masks for high-resolution photolithography fully exploiting the advantage of the smallness of the clusters, 0.7 nm in diameter. It has been found also that electron irradiation causes structural changes in C_{60} films which makes it promising to use C_{60} films as a resist material for electron-beam (EB) lithography. In fact, Robinson *et al.* showed that C_{60}-derived polymer films have a high sensitivity practically enough for resist patterning on 10 nm scale with a focused 20 keV electron

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beam of ordinary EB scanners [1]. In spite of its importance, little is known about the nature of the structural changes induced by electron beam irradiation. We previously reported the polymerization of C_{60} clusters in C_{60} films grown on Si substrates that is induced by injection of tunneling electrons from STM tips [2]. We found that the polymerization caused by the electron injection was assisted by compressive internal strain, and also that the polymerization effect spreads over a distance of 10 nm from the injection point, in an extent very similar to that observed in the tunneling-injection-enhanced Cl atom jumps on Si surfaces we found previously [3].

In this paper, we demonstrate that this spreading effect depends on the strain state of the C_{60} films grown on different substrates, Si and HOPG (highly oriented pyrolytic graphite). Experiments revealed that the spreading effect was considerably reduced in the films grown on HOPG substrates that are probably less compressively strained.

EXPERIMENTAL PROCEDURE

Single crystalline face-centered-cubic C_{60} films in thickness of several monolayers were grown by molecular beam epitaxy at room temperature evaporating 99.99% C_{60} powder in ultrahigh vacuum (UHV) either onto Si (111)-(7×7) substrates or onto (0001) cleavage surfaces of HOPG cleaned by baking under the pressure of 1×10^{-8} Pa. STM experiments were conducted at 5×10^{-9} Pa by using an STM (JEOL, JSTM4500XT) with tungsten tips fabricated by a laboratory-built electrochemical etching apparatus [4].

RESULTS

The typical STM images of C_{60} films grown on an HOPG substrate and on a Si substrate are shown in Figure 1(a) ($V_S = 1.5$ V, $I_T = 50$ pA) and (b) ($V_S = 4.0$ V, $I_T = 50$ pA), respectively. While the C_{60}/Si film contains many steps terminating with misfit dislocations indicated by arrows, the surface of C_{60}/HOPG film appears much less defective other than monolayer steps. Figures 1(c) and 1(d) are enlarged images of the regions marked with squares in Figure 1(a) and (b), respectively, demonstrating that the surface of the C_{60}/HOPG is flat and uniform compared to C_{60}/Si which is wavy as shown by the line profiles in Figure 1(e). The electron-injection-polymerization experiments on the two types of samples revealed that the polymerization rate in C_{60}/Si samples is generally quite dependent on the sample position whereas the positional dependence of the polymerization rate in C_{60}/HOPG samples is small. Also, the polymerization rate was found to be systematically lower in the C_{60}/HOPG samples than the C_{60}/Si samples.

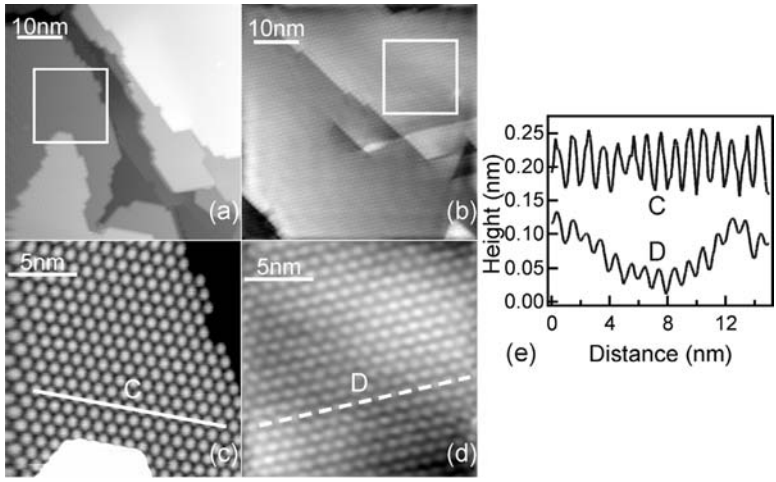

FIGURE 1 STM images of C_{60} film surfaces grown on HOPG substrate ((a) and (c)) and on Si substrate ((c) and (d)). Figure (e) shows topographic profiles along the solid line C and the dotted line D.

To investigate how to intentionally localize the effects of electron-injection-polymerization, we conducted the following experiments; (1) STM imaging a sample area of about $40\,\text{nm} \times 40\,\text{nm}$ in size, (2) injecting electrons by scanning a small area at the center of the imaged frame, and (3) STM imaging the same region again. The typical results thus obtained for C_{60}/Si films and C_{60}/HOPG films are shown in Figure 2(a) ($V_S = 1.5\,\text{V}$,

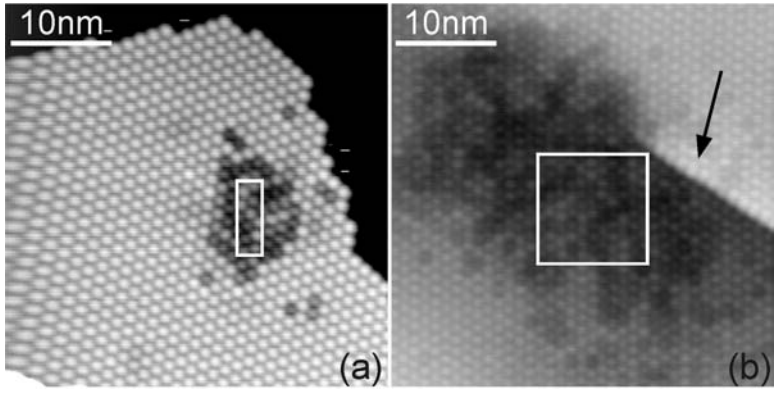

FIGURE 2 Spreading of electron injection effects (a) on C_{60}/HOPG ($V_S = 1.5\,\text{V}$, $I_T = 50\,\text{pA}$) and (b) on C_{60}/Si ($V_S = 4.0\,\text{V}$, $I_T = 50\,\text{pA}$).

$I_T = 50\,pA$) and 2(b) ($V_S = 4.0\,V$, $I_T = 50\,pA$), respectively, where the square marks indicate the areas of electron injection for 18 s at $V_S = +4.2\,V$ and $I_T = 0.1\,nA$. The clusters in dark contrast exhibiting internal structures are considered to be rotation-frozen C_{60} clusters polymerized with underlying clusters by the electron injection. Figures 2(a) and 2(b) indicate that in both kinds of samples, the electron injection effects spread in space from the injection areas, but the size of spreading in C_{60}/HOPG films was a few nm, considerably smaller than that ($\sim$10 nm) in C_{60}/Si films.

DISCUSSION

Previously, we reported [2] that the polymerization on C_{60}/Si films is enhanced by compressive strains, which is the main cause of the positional dependence of the polymerization efficiency. The films deposited on HOPG substrates are relatively homogeneous and may be unstrained because of the weak interaction between C_{60} clusters and the HOPG substrates while those films on Si substrates are more or less heterogeneously strained. Due to the homogeneous and less compressively strained state in the C_{60}/HOPG films, the positional dependence of the polymerization efficiency is weaker and the polymerization rate is lower.

The electron injection effect spread beyond monolayer step edges (not shown) while the spreading effect is blocked by the surface step indicated by an arrow in Figure 2(b), a step with a partial cluster height formed at an intersection of stacking fault planes with the surface. These facts that the electron injection effect spreads from the injection point beyond perfect step edges accompanying no other defects but is blocked by planar defects like stacking faults strongly suggest that the fundamental excitations induced by the electron injection could propagate along three dimensional band states associated with the ordered crystalline C_{60} lattice. In this framework, the electronic excitation caused by the electron injection can more easily propagate when the separation of the adjacent clusters is shortened in compressed films like C_{60}/Si. Also from this model, we could expect that the introduction of defects or amorphization at its extreme would suppress the spreading effect and hence improve the spatial resolution in lithography.

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