

## Selective Adsorption of $C_{60}$ on Ge/Si Nanostructures

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Selective adsorption of  $C_{60}$  on nanoscale Ge areas can be achieved, while neighboring Si(111) areas remain uncovered, if the whole surface is initially terminated by Bi. Fullerene chemisorption is found at Bi vacancies which form due to partial thermal desorption of the Bi surfactant. The growth rate and temperature dependence of the  $C_{60}$  adsorption were measured using scanning tunneling microscopy and are described consistently by a rate equation model. The selectivity of the  $C_{60}$  adsorption can be traced back to an easier vacancy formation in the Bi layer on top of the Ge areas compared to the Si areas. Furthermore, it is also possible to desorb  $C_{60}$  from Ge areas, allowing the use of  $C_{60}$  as a resist on the nanoscale.

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Nanostructuring using epitaxial growth processes can lead down to sizes in the single digit nanometer range or even ultimately to the single molecule or atom range which is not accessible by lithography. Serious challenges in these efforts are size fluctuations during the growth process and the ability to place self-assembled nanostructures at desired positions. However, in some cases it has been possible to grow nanowires of Fe or organic molecules using regularly stepped Si surfaces as templates [1,2]. A great help in these nanostructuring attempts is the ability to directly inspect the nanostructure formation by chemically sensitive surface imaging techniques. For instance, in our previous studies it has been shown that the use of Bi as a surfactant [3,4] not only largely suppresses Si/Ge intermixing but also allows the distinction between Si and Ge on the nanometer scale [5,6]. Using a step flow growth mode during Bi mediated Ge epitaxy on a vicinal Si(111) substrate, we successfully fabricated an array of 4 nm wide one atomic layer high Ge nanowires [7]. These nanowires are quite appealing from the structural point of view and could serve as templates for growth of even more complicated nanostructures based on different material combinations (e.g., metal on semiconductor). However, attempts to either desorb Bi selectively from Ge areas or decorate the Ge nanowires by a metal have failed so far [8]. The fundamental reason for this lack of selectivity is that Si and Ge are, in fact, chemically very similar materials. To achieve the selectivity a physical mechanism has to be found that would enhance the material difference.

In this Letter we show that the use of surfactants is a means to control the selectivity of  $C_{60}$  adsorption and leads to new nanostructuring opportunities. Deposition of  $C_{60}$  on a Bi-terminated surface results in selective replacement of Bi by  $C_{60}$  in Ge surface areas [Fig. 1(a)]. Our analysis

shows that the high selectivity of  $C_{60}$  adsorption is made possible due to a complex mechanism of  $C_{60}$  adsorption, involving the formation of vacancies in the Bi layer followed by vacancy-mediated chemisorption of  $C_{60}$  on Ge surface areas only.

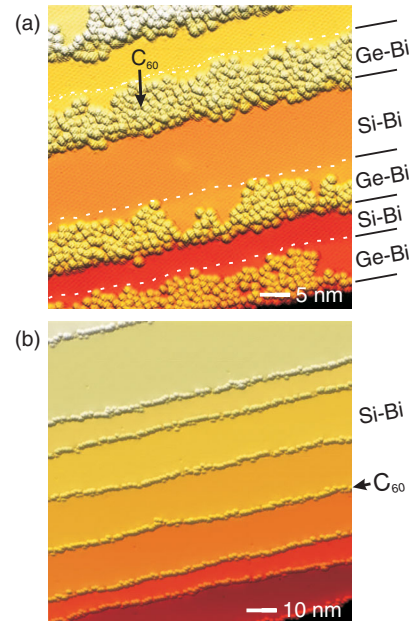


FIG. 1 (color online). (a) Selective growth of  $C_{60}$  on Ge areas, while Si areas remain uncovered. The slight height difference between Si and Ge areas is highlighted by dashed lines at the Si/Ge boundaries. The  $C_{60}$  are seen as round protrusions with intramolecular structure on the Ge areas. (5 ML  $C_{60}$  deposited at  $T = 440^\circ\text{C}$  during 10 min) (b) Selective adsorption of  $C_{60}$  at Si step edges (2 ML  $C_{60}$  deposited at  $T = 420^\circ\text{C}$  during 10 min).

In our experiments a Bi-terminated Si(111) surface was prepared by adsorbing one atomic layer of Bi (1 ML Bi corresponds to  $7.8 \times 10^{14}$  atoms/cm<sup>2</sup>) on the clean Si(111) – (7 × 7) as described in [7]. Then a submonolayer amount of Ge (1 ML Si or Ge corresponds to  $1.56 \times 10^{15}$  atoms/cm<sup>2</sup>) was deposited. During Ge growth Bi floated up at the surface as usual in surfactant mediated growth [4]. A Bi flux was maintained during Ge growth in order to keep a 1 ML Bi termination. C<sub>60</sub> was evaporated from a Knudsen cell. Upon the growth the surface was imaged with STM.

Figure 1(a) shows an STM image of a Si(111) sample on which Ge nanowires have been grown at step edges using Bi mediated epitaxy. The borders between the Si and the Ge areas (each with 1 ML Bi on top), which show different apparent heights in the STM images [5,6], are highlighted by dashed lines. Subsequently 5 ML of C<sub>60</sub> were deposited onto this Ge nanowire template at a temperature of 440 °C. As seen in Fig. 1(a) only a small fraction of the deposited 5 ML of C<sub>60</sub> actually remains on the surface whereby C<sub>60</sub> adsorbs selectively on the Ge areas. The selectivity is perfect in the sense that virtually no C<sub>60</sub> adsorbs on the Si; however, the Ge nanowires are not completely covered by C<sub>60</sub>. When no Ge area is present on the surface, deposition of C<sub>60</sub> on Bi/Si(111) leads to selective adsorption of C<sub>60</sub> at the Si step edges [Fig. 1(b)].

In order to identify the reason for the selective adsorption of C<sub>60</sub> on Ge areas we analyzed the C<sub>60</sub> adsorption as a function of temperature, which shows a different behavior on the surfactant terminated surface than on clean Si or Ge [9,10]. The results are summarized schematically in Fig. 2. At room temperature C<sub>60</sub> adsorbs on top of the Bi layer and forms large two-dimensional islands consisting of well-ordered hexagonally arranged C<sub>60</sub> molecules. The

observed height of the C<sub>60</sub> islands above the Bi layer of  $\sim 8$  Å is close to the distance between the (111) planes in a bulk fullerite (8.15 Å [11]), which suggests a weak van der Waals bonding of C<sub>60</sub> to Bi/Ge/Si(111) and Bi/Si(111) surfaces. In this weakly bound physisorption state C<sub>60</sub> shows no selectivity and grows both on Si and on Ge areas. After short annealing at 200 °C the physisorbed C<sub>60</sub> layer completely desorbs, restoring the Bi covered surface. Depositing C<sub>60</sub> in a temperature range of 200–400 °C does not lead to any adsorption of C<sub>60</sub> [Fig. 2(b)].

At temperatures above 420 °C adsorption of C<sub>60</sub> could be seen on Ge, and starting from about 460 °C also on Si terraces [12], leading to a complete coverage of C<sub>60</sub> on the Ge and Si areas. At Si step edges the adsorption occurs already at somewhat lower temperatures, cf. Fig. 1(b). However, in this high temperature range the adsorption mechanism differs considerably from that observed at room temperature. At submonolayer surface coverages most of the C<sub>60</sub> adsorb either as single molecules, or forming small irregular clusters. The measured apparent height of the C<sub>60</sub> above the surrounding Bi layer is only 4 Å which is much smaller than the  $\sim 8$  Å measured for the physisorbed C<sub>60</sub>, suggesting that at elevated temperatures C<sub>60</sub> adsorbs directly to Si (Ge), i.e., without Bi below C<sub>60</sub> [Fig. 2(c)]. The irregular arrangement of the C<sub>60</sub> clusters hints at the strong covalent bonding of C<sub>60</sub> to the underlying Si (Ge) surface, in agreement with results of studies on C<sub>60</sub> adsorption on clean Si(111) and Ge(111) surfaces [13].

Direct bonding of C<sub>60</sub> to Si and Ge surfaces may occur either at vacancies in the Bi layer or via displacement of Bi atoms by C<sub>60</sub>. In the following we will present an experimental proof of the vacancy-mediated chemisorption of C<sub>60</sub> on the Bi-terminated Si(111) surface. In control experiments we deposited the same amount of C<sub>60</sub> in two different ways. In the first experiment, 1.3 ML of C<sub>60</sub> was deposited continuously for 5 min at 480 °C, while in the second experiment the sample was first annealed for 5 min at 480 °C and then the same amount of C<sub>60</sub> was deposited in a burst of only 10 sec at a low temperature of 350 °C. STM images of the surface after C<sub>60</sub> deposition in the first and the second experiment are shown in Figs. 3(a) and 3(b), respectively. As can be seen, both the amount of C<sub>60</sub> that actually stick to the surface (approximately 0.3% of the deposited 1.3 ML) and the density of C<sub>60</sub> clusters (4500 μm<sup>-2</sup>) are almost identical in both cases. This indicates that the annealing phase lasting the same time as the continuous deposition experiment, determines the island density and not the actual C<sub>60</sub> deposition which was performed at a 30 times higher deposition rate.

The major effect of the annealing is a partial desorption of Bi and formation of vacancies in the Bi layer which can be directly seen in an STM image of the surface after merely annealing for 5 min at 480 °C [Fig. 3(c)]. Therefore, we conclude that the chemisorption of C<sub>60</sub>

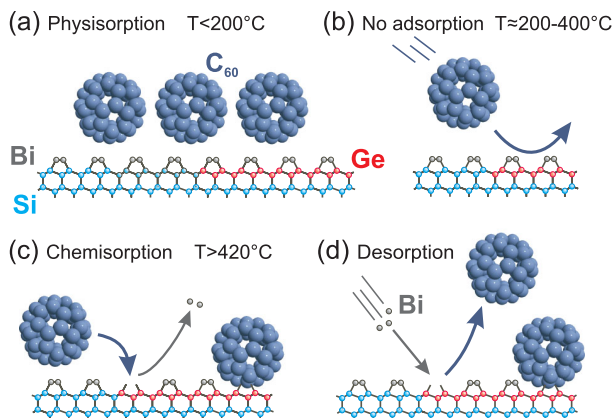


FIG. 2 (color online). Schematic of the C<sub>60</sub> adsorption on Si (Ge) as a function of temperature. (a) At room temperature C<sub>60</sub> adsorbs in a weakly bound physisorption state on top of the Bi layer. (b) At 200–400 °C no C<sub>60</sub> adsorption occurs. (c) Above 420 °C chemisorption of C<sub>60</sub> occurs at Bi vacancies on Ge. (d) Under Bi flux C<sub>60</sub> desorbs from the Ge surface.

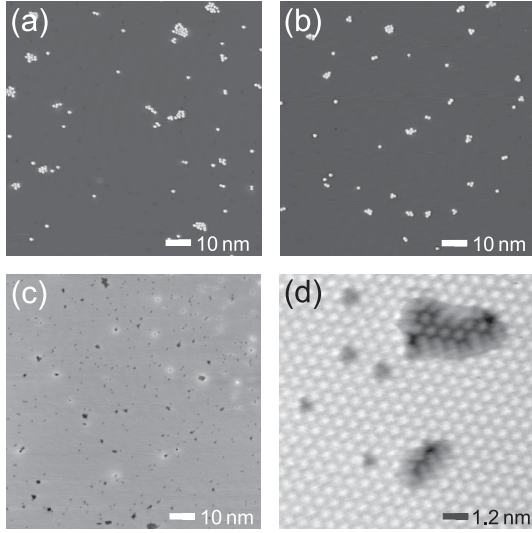


FIG. 3. (a) Formation of 2D  $C_{60}$  islands on a Bi covered Si (111) surface during continuous deposition (1.3 ML  $C_{60}$  deposited at  $T = 480^\circ\text{C}$  during 5 min). (b) Two step deposition consisting of annealing at  $T = 480^\circ\text{C}$  for 5 min and then a burst deposition of  $C_{60}$  for 10 sec (1.3 ML  $C_{60}$  deposited at  $T = 350^\circ\text{C}$ ). This leads to the same island density as in (a). (c) Formation of Bi vacancies after annealing for 5 min at  $T = 480^\circ\text{C}$ . (d) Single vacancies and vacancy islands in the Bi layer created by 15 min annealing at  $T = 480^\circ\text{C}$ .

occurs at vacancies in the Bi layer which are formed by thermal desorption of Bi.

A more detailed analysis of the vacancies shows that there are single vacancies where only one Bi trimer of the  $\sqrt{3} \times \sqrt{3}$  Bi reconstruction has converted to a Bi monomer, as well as small vacancy islands with more Bi trimers reduced to the  $1/3$  ML coverage Bi monomer phase [Fig. 3(d)]. The density of the observed vacancy islands corresponds well to the density of  $C_{60}$  single molecules plus  $C_{60}$  clusters observed in the experiments shown in Figs. 3(a) and 3(b); therefore, we conclude that one missing Bi trimer is not enough to trigger  $C_{60}$  adsorption, but larger vacancies are needed as nucleation centers for  $C_{60}$ .

As an additional check for the proposed adsorption mechanism of  $C_{60}$  on Bi/Si(111) we have performed  $C_{60}$  deposition under the same conditions as in the experiment shown in Fig. 3(a) but supplying a Bi flux to prevent Bi desorption. In this case the formation of Bi vacancies is inhibited (deposited Bi fills the vacancies), and the vacancy-mediated  $C_{60}$  chemisorption should be suppressed. The control experiments confirmed this prediction.

Selective adsorption of  $C_{60}$  at Si step edges observed on Bi/Si(111) at  $420^\circ\text{C}$  [Fig. 1(b)] is also in agreement with the proposed vacancy-mediated adsorption mechanism. As has been shown in a previous study, Bi desorbs from the upper side of the Si step edges at temperatures for which the Bi termination of the Si(111) terraces is still maintained

[7]. This allows  $C_{60}$  molecules to bind covalently to Si forming one-dimensional chains at the descending Si steps.

Based on the experimental observations the following model of the high temperature submonolayer growth of  $C_{60}$  on Bi-terminated Si(111) and Ge(111) surfaces is proposed.  $C_{60}$  molecules arriving at the surface with the incoming flux  $F$  first adsorb in a weakly bound physisorbed (precursor) state on top of the Bi layer. The physisorbed  $C_{60}$  molecules are very mobile as can be seen from the low density and large size of the islands formed on Bi/Si(Ge)/Si(111) at room temperature deposition. From the precursor state  $C_{60}$  can either desorb or go to the chemisorbed state by finding a vacancy island in the Bi layer where  $C_{60}$  can bind directly to the Si(Ge) surface. Alternatively the  $C_{60}$  can attach to an already existing chemisorbed  $C_{60}$  island by displacing chemisorbed Bi to its precursor state on top of the Bi layer. Since chemisorption immobilizes  $C_{60}$ , a single chemisorbed  $C_{60}$  molecule represents a stable nucleus which can grow further by capturing more migrating precursor molecules. The rate of nucleation of the  $C_{60}$  islands (i.e., of single chemisorbed  $C_{60}$  molecules plus  $C_{60}$  clusters) is therefore given by the rate of filling the Bi-vacancy islands by  $C_{60}$  precursors.

To confirm the proposed adsorption mechanism we have constructed a rate equations model describing the  $C_{60}$  nucleation kinetics. The rate equations are expressed in terms of spatially uniform densities of precursor  $C_{60}$  molecules on top of the Bi layer  $n$ , single Bi vacancies  $n_v$ , vacancy islands  $N_v$ , and  $C_{60}$  islands  $N$ . These equations relate the experimentally observable macroscopic quantities, such as  $N$ , with the kinetic rates of atomic scale surface processes:

$$\frac{dn}{dt} = F - J_{\text{des}} - DnN_v - D^*nN \quad (1)$$

$$\frac{dn_v}{dt} = k_v - G_v \quad (2)$$

$$\frac{dN_v}{dt} = G_v - DnN_v \quad (3)$$

$$\frac{dN}{dt} = DnN_v. \quad (4)$$

Here  $F$  and  $J_{\text{des}}$  are the  $C_{60}$  deposition and desorption fluxes, respectively,  $D$  is the attachment rate of a precursor  $C_{60}$  to a Bi-vacancy island,  $D^*$  is the attachment rate of a precursor  $C_{60}$  to an existing  $C_{60}$  island,  $k_v$  is the formation rate of single Bi vacancies, and  $G_v$  is the formation rate of vacancy islands. Writing Eqs. (2) and (3) we assumed rapid desorption of Bi adatoms adsorbed on top of the Bi layer and therefore neglected the terms describing the refilling of single vacancies and vacancy islands by Bi adatoms. It follows from Eqs. (2)–(4) that in a steady state the  $C_{60}$  islands nucleate at the same rate as new single Bi vacancies form, and the steady-state density of  $C_{60}$  islands is given by



$$N \sim t \exp(-E/k_B T). \quad (5)$$

Here  $t$  is the deposition time,  $T$  is the substrate temperature, and  $E$  is the activation energy for the creation of a single vacancy in the Bi layer. Bearing in mind that the vacancy islands have a Bi monomer structure, as shown in Fig. 3(d), we assume the Bi trimer dissociation together with the transfer of two Bi atoms to a weakly bound adsorption state on top of the Bi layer as the rate limiting step for the vacancy formation and associate the activation energy  $E$  with this process.

It follows from Eq. (5) that the total density of single  $C_{60}$  molecules plus  $C_{60}$  clusters chemisorbed on the Bi-terminated Si(111) or Ge(111) surface,  $N$ , should not depend on the  $C_{60}$  deposition rate and should obey an Arrhenius-type temperature dependence increasing with increasing substrate temperature. The increasing temperature dependence of the  $C_{60}$  island density is in contrast to the predictions of standard nucleation theories [14], and is directly related to the proposed vacancy-mediated nucleation mechanism of  $C_{60}$ . Here higher temperatures mean a higher rate of vacancy formation, and, hence, higher  $C_{60}$  island density. The experimental rate and temperature dependences of the density of  $C_{60}$  islands on Bi/Si(111) are shown in Figs. 4(a) and 4(b) and agree with the predictions of Eq. (5). Good agreement of the experimentally measured flux and temperature dependencies of the  $C_{60}$  island densities with that predicted by rate equations confirm the proposed atomistic mechanism of the  $C_{60}$  adsorption. A slight increase of the  $C_{60}$  island density with the deposition flux  $F$  seen in Fig. 4(a) indicates that our assumption of the balance between the Bi-vacancy creation and filling by  $C_{60}$  is only approximately fulfilled and for lower fluxes some of the Bi vacancies are refilled by Bi adatoms, inhibiting the  $C_{60}$  chemisorption.

An Arrhenius-type temperature dependence was also found for the  $C_{60}$  island density on Ge(1 ML)/Si(111) as shown in Fig. 4(b). By fitting the experimentally measured  $C_{60}$  island densities with Eq. (5) we obtain a much higher vacancy formation energy for Bi on Si ( $3.2 \pm 0.3$  eV) than for Bi on Ge ( $1.7 \pm 0.3$  eV). This finally explains the selectivity of the  $C_{60}$  chemisorption. One can tune the temperature to a range ( $T_{\text{sel}}$ ), such that Bi-vacancy formation occurs readily at the Ge areas, leaving Bi vacancies which can serve as nucleation centers for  $C_{60}$ , while on the neighboring Si areas the activation energy for a Bi-vacancy formation is so high that no Bi vacancies form at  $T_{\text{sel}}$ . There might be also additional factors that enhance  $C_{60}$  adsorption selectivity even further. For instance, Bi desorption energy from the top of the Bi layer on Si might be higher than from the Bi layer on Ge. In this case the density of Bi precursors will be larger on the Si areas suppressing the vacancy formation there.

In order to use  $C_{60}$  as a resist in further nanostructuring attempts it is necessary to be able also to remove it from the surface after use. Simple annealing did not result in a

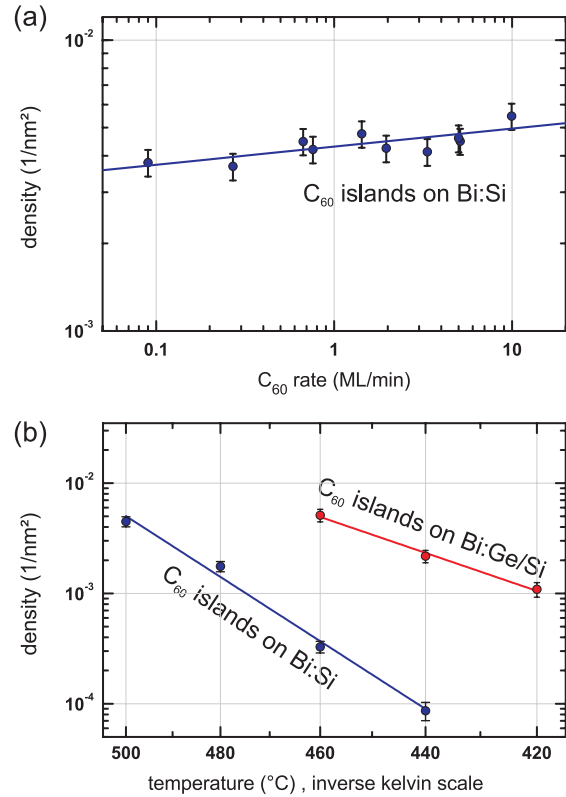


FIG. 4 (color online). Rate dependence (a) and temperature dependence (b) of the  $C_{60}$  island density on a 1 ML Bi/Si(111) surface. In (b) additionally the  $C_{60}$  island density on a Bi:Ge/Si(111) surface is shown. The smaller slope indicates a lower vacancy formation energy for Bi on Ge than for Bi on Si. Growth conditions where (a) deposition at 480  $^{\circ}\text{C}$  for 5 min, (b) 0.8 ML  $C_{60}$  during 2 min. The error bars were estimated from the counting statistics and an assumed error of 10% for the measurement of the area due to the nonlinearity of the piezo elements.

desorption; however, annealing of a  $C_{60}$  covered Ge(1 ML)/Si(111) surface at 420  $^{\circ}\text{C}$  in a flux of Bi (4 ML/min) leads to a desorption of  $C_{60}$  [12] according to the mechanism sketched in Fig. 2(d). The Bi substitutes the  $C_{60}$  and fills the vacancies in the Bi termination layer. An almost complete  $C_{60}$  desorption can be achieved, leaving less than 1% of the  $C_{60}$  bound to the surface. This occurs probably because the remaining  $C_{60}$  bond to Si, since due to some residual Ge/Si intermixing a small amount of Si is also present at a nominally Ge covered surface [6]. On the other hand  $C_{60}$  chemisorbed on a Si(111) surface cannot be desorbed, with or without Bi flux. While annealing to temperatures up to 650  $^{\circ}\text{C}$  leaves the  $C_{60}$  on Si(111) unchanged, annealing beyond 700  $^{\circ}\text{C}$  leads to a decomposition of the  $C_{60}$ , as already reported previously [15].

In conclusion, selective adsorption of  $C_{60}$  at Ge areas and at Si step edges has been achieved. The mechanism for the selective adsorption is the nucleation and growth of  $C_{60}$

at Bi vacancies which form preferentially on Ge areas due to the lower vacancy formation energy compared to Si, as revealed by our growth model. It is possible to selectively cover Ge nanowire templates, with C<sub>60</sub> (and to remove it afterwards) in order to use C<sub>60</sub> as a resist in further nanostructuring steps.

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