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Self-assembly of Ge clusters on highly oriented pyrolytic graphite surfaces

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ABSTRACT

The self-assembly of Ge clusters on highly oriented pyrolytic graphite (HOPG) was investigated by depositing Ge at various temperatures, using *in situ*-scanning electron microscopy under an ultrahigh vacuum. At the first stage of Ge deposition, Ge clusters were formed along the steps on the HOPG surfaces. With an increase in the amount of Ge deposited, nanostructures of Ge self-assembled depending on the deposition temperature used. At room temperature, the Ge clusters merged together, resulting in the formation of dendritic-shaped structures. At high temperatures (200–600 °C), chain structures of Ge clusters were formed along the steps on the HOPG surfaces. The density of the Ge clusters comprising the chains along the chain direction decreased with an increase in the deposition temperature. This can be explained by the diffusion length of the Ge atoms along the steps during chain formation. From this result, an activation energy of ~0.12 eV was determined for the diffusion of the Ge atoms along the HOPG steps. Ostwald ripening of the Ge clusters was also observed by annealing the chain structure of the Ge clusters. By analyzing the change in the Ge cluster density in the chains, an activation energy of ~0.68 eV was obtained for a movement of Ge cluster periphery by attachment and detachment of Ge atoms.

1. Introduction

The self-assembly of semiconducting nanostructures has drawn much attention because of their interesting properties such as the quantum confinement effects [1–6] and characteristic optical properties [7–10]. The growth of metal and semiconductor nanostructures on inert substrates like highly oriented pyrolytic graphite (HOPG) has been studied to investigate the intrinsic properties of nanostructured materials [11–15]. Clean HOPG substrate surfaces are easy to prepare by cleavage in the air. The surfaces are chemically inert and compose atomically flat terraces that spread over several 100 nm between atomic steps. The weak interactions between the HOPG and nanostructures on its surface cause the intrinsic properties of the nanostructures to appear. X-ray photoelectron spectroscopy on bismuth on a HOPG surface showed a similar binding energy to that of bulk bismuth [13]. For the group IV semiconductor Si, growth of Si nanostructures on HOPG surfaces has been studied [14]. In this paper, we focus on Ge on HOPG surfaces because Ge is a commonly used semiconductor material used for many purposes, such as high mobility channel materials for field-effect transistors [16] and optical devices with quantum wells [17] or dots [18,19]. However, there are only a few studies that have focused on Ge nanostructures on HOPG surfaces [20]. Studies were carried out on the growth of Ge nanostructures on HOPG surfaces for films deposited at room temperature (RT), where quasi-one-dimensional (1D) Ge nanowires were formed. The temperature dependence of the growth elucidates the growth mechanism of the nanostructures in general. Then, in this study, the growth mechanism of Ge nanostructures was investigated by forming Ge nanostructures on HOPG surfaces under various conditions: various temperatures and deposition amounts. The growth of the Ge nanostructures was determined by the diffusion of Ge atoms along the HOPG surface step edges.

2. Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) chamber at a base pressure of ~1×10^{-8} Pa. The UHV chamber was equipped with a scanning electron microscope (SEM) and a Knudsen-cell for Ge deposition. Details on the equipment were described elsewhere [21]. Clean HOPG substrates were prepared by cleaving in air and immediately transferring them into the UHV chamber [22]. HOPG substrates were degassed for surface cleaning at ~1000 °C in the UHV chamber for several hours. Ge was deposited onto the cleaned HOPG surfaces at various temperatures from RT to 600 °C. During Ge deposition, the pressure in the UHV chamber was maintained below 5.0×10^{-9} Torr. The Ge deposition rate was 0.24 nm/min. The deposition amount of Ge was referred to as the nominal thickness. Heating was conducted by passing an electric current through the HOPG substrates (e.g. ~4 A at 600 °C, ~13 A at 800 °C). Temperature

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was measured by radiation thermometer. After Ge deposition, *in situ* observations of the sample surfaces were performed by SEM.

3. Results and discussion

3.1. Growth of Ge clusters on HOPG surfaces

Fig. 1(a) and (b) shows SEM images of HOPG samples after 5 nm of Ge was deposited at RT and 400 °C, respectively. The bright contrast regions correspond to the deposited Ge atoms. In the case of RT deposition (Fig. 1(a)), deposited Ge atoms spread from the steps to the terraces, leading to the formation of dendritic shapes that looked to be composed of Ge clusters, similar to Au/HOPG [23]. In addition to the dendritic-shaped structures, on the terrace, "flower-shaped" Ge structures also appeared as shown by the arrow in Fig. 1(a). The flower-shaped structure on the terrace was reported in the previous scanning tunneling microscopic (STM) study [20] where Ge deposition amount is small (1.8 nm). For high deposition temperatures (200–600 °C), bright lines were observed along the surface steps. The bright lines in Fig. 1(b) were the chain structures of the Ge clusters and the clusters positioned only at the HOPG surface steps.

To investigate the growth of the dendritic-shaped Ge structures, various amounts of Ge were deposited on HOPG surfaces at RT. Figs. 1(a), 2(a), and (b) show the surface morphologies of 3–10-nm-thick Ge deposited on HOPG surfaces at RT. Fig. 2(a) shows that Ge clusters only appeared on the step edges initially. Some of the Ge clusters were observed on the terraces, which were presumably stabilized by surface defects or impurities to form the flower-shaped structures. With an increase in the amount of Ge deposited, Ge cluster structures spread from initially-formed clusters at the step sites onto the terraces, resulting in dendritic-shaped Ge structures. In 10 nm Ge deposition, the HOPG surfaces were mostly covered by dendritic-shaped Ge structures.

The growth of the chain structures of the Ge clusters was also investigated. Figs. 1(b), 2(c), and (d) show Ge clusters formed by deposition of 3–10-nm-thick Ge at 400 °C. The Ge clusters formed on the edges of the steps and there were no Ge clusters on the terraces for all deposition stages. This indicated that step edges work as nucleation sites mainly. Fig. 3(a)–(c) shows detailed SEM images of Ge cluster chains, which were formed by depositing 5-nm-thick Ge at 200, 400, and 600 °C. Enlarged images (white rectangles) are shown in all of the SEM images. These images demonstrated that the chain structures of the round Ge clusters were formed by 1D alignment of the Ge clusters with certain separations. The 1D density of the Ge clusters, defined as the inverse of the Ge cluster separation, is shown in Fig. 3(d).

According to the previous paper [20], Ge structure formed at RT has amorphous structures, and its amorphous Ge was crystallized by annealing. High temperature formation has not been investigated in the previous STM study [20]. On the basis on these results, our Ge structures formed at high temperatures were considered to be crystals. As for the relation of crystal orientation between Ge clusters and substrates, further study is needed.

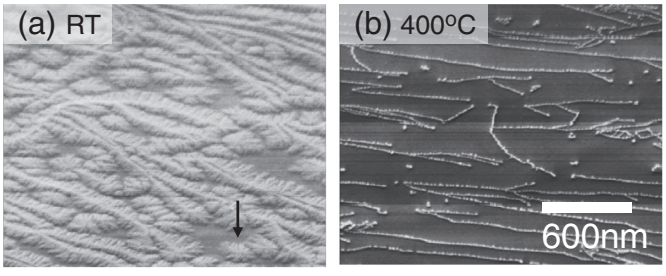

Fig. 1. SEM images after 5 nm of Ge was deposited on HOPG surfaces at (a) RT and (b) 400 °C.

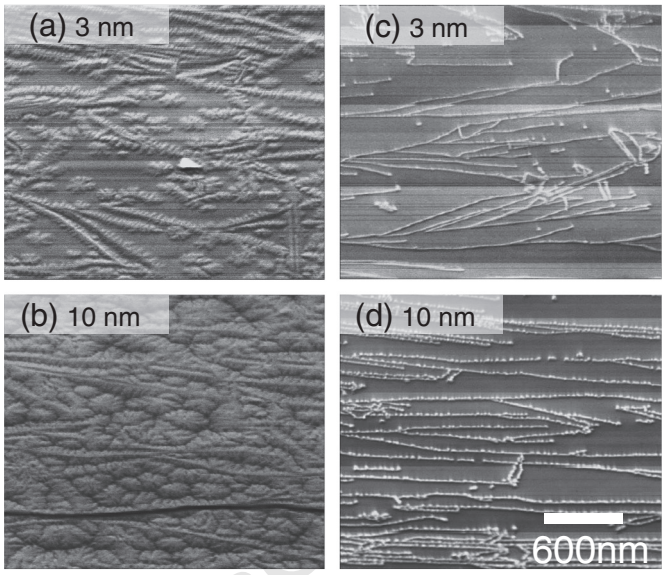

Fig. 2. SEM images after deposition of various amount of Ge on HOPG (a, b) at RT and (c, d) at 400 °C. Deposition amounts were 3 nm (a, c) and 10 nm (b, d).

At the first stage of Ge deposition, Ge clusters formed on the step edges of the HOPG surfaces for all the deposition temperatures. This indicated that the Ge atoms accumulated at the trap sites, such as step edges, caused by the inertness of the HOPG surfaces after the Ge atoms diffused through the surface. At RT, we observed dendritic-shaped Ge structures. The mechanism of dendritic growth on the surface in general case has been studied as follows [24]. Atom was initially trapped at some site, and worked as the origin of the structure. This was followed by the random work of other atoms and their trap at the adjacent sites to already-trapped atoms to form random structures. We adopted the similar mechanism that initially-trapping sites were step edges, and then, fractal structures grew on the terraces by the above-mentioned random aggregation [24] resulting in the dendritic shapes.

At high temperature, Ge atoms were only stabilized at the step edges presumably due to high evaporation probability on the terrace despite further Ge deposition. After trap of Ge atoms at the step edges, Ge atoms diffused along the step edges where evaporation effect was reduced, and then Ge clusters were formed. At high temperatures, the Ge atoms involved in the Ge cluster growth were the atoms that diffused along the step sites after some of surface Ge atoms were trapped at the step edges prior to the evaporation. In this scenario, shown in Fig. 3(e), separation of the Ge clusters in chain structures, seen in Fig. 3(d), was related to the diffusion length of the Ge atoms along the step edges. In the diffusion model for cluster growth, the density of clusters, n, can be written as [25]:

$$n = \frac{1}{L} \propto \exp\left(\frac{E_d}{4k_B T}\right), \tag{1}$$

where L is the Ge cluster separation, E_d is the activation energy for diffusion along the step edge, K_B is Boltzmann constant, and T is an absolute temperature. The 1D density of the Ge clusters was fitted with Eq. (1), shown by the dotted lines in Fig. 3(d), and E_d was estimated to be 0.12 ± 0.01 eV. This value is comparable to that of Ag deposited on HOPG, where the activation energy for diffusion along the steps was reported to be 0.14 ± 4.05 eV [26]. In addition, for Au particles deposited on HOPG surfaces at RT, dendritic shapes were formed on the surfaces. The activation energy for the surface diffusion was 0.24 eV [23]. The studies focused on the diffusion of Ge atoms on Si [14,27,28], not on HOPG. The activation energy for Ge atom diffusion into Si was estimated to be 0.65 eV [27]. In another report with Ge on a SiGe buffer layer on Si,