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Germanene: Experimental Study for Graphene Like Two Dimensional Germanium

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Inspired by the fruitful results based on graphene, two dimensional structures of group-IV elements (Si, Ge) are currently the most investigated materials in physics and nano science. Silicene, the silicon analogy of graphene, had already been synthesized experimentally, but the germanium analogy of graphene has not been synthesized experimentally yet. Only a few theoretical works predicted that graphene like 2-D honeycomb structure of germanium is stable with low buckling. We experimentally observed the phase evolutions for germanium growth on Ag(111) by low energy electron diffraction. We observed that the phase evolutions were strongly dependent on the amount of germanium coverage on Ag(111). We obtained a $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern by germanium adsorption on Ag(111) at RT and the pattern become clear after annealing at 415 K. The $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern is analogous to the $(6\sqrt{3} \times 6\sqrt{3})R\,30°$ pattern of graphene formation on SiC(0001). We also observed the atomically resolved STM image after one monolayer germanium adsorption on Ag(111). By the observation on the STM image, we observed a honeycomb structure and by further close observation on larger area, we observed the $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ moiré structure. On the basis of the LEED and STM results, we have proposed an atomic model for germanene, the germanium analogy of graphene, growth on Ag(111).

Keywords: Ge, Ag(111), germanene, LEED, STM

1. Introduction

In the past decade graphene has emerged as two dimensional system for both fundamental research and novel applications including electronic devices, energy storages, and transparent protection layers[1-4]. Inspired by the fruitful results based on graphene, two dimensional structures of group-IV elements (Si, Ge) are currently the most investigated materials in physics and nano science. Now-a-days, silicene[5,6], the silicon analogy of graphene, has already drawn strong theoretical and experimental attention. Some groups have synthesized silicene experimentally[7-11]. But the counter part of germanium, germanene, the germanium analogy of graphene in which Ge atoms replace C atoms in a two dimensional honeycomb lattice, has not been synthesized experimentally yet. Only a few theoretical works have been done on the two dimensional honeycomb structure of germanium. For example, Cahangirov et al.[12], using density functional theory, have shown that a quasi-two dimensional structure of germanium is stable with low buckling, where the buckling value is 0.064 nm. They reported that the Ge-Ge nearest-neighbor distance is 0.238 nm, slightly reduced from that of bulk (0.245 nm). They also reported that the electronic band structure of the quasi-two dimensional honeycomb germanium showed linear band crossing across the Fermi level at Brillouin zone boundaries, which means that it processes Dirac cones. Liu et al.[13] also reported that the two-dimensional honeycomb structure of germanium is stable with low buckling and they mentioned the nearest neighbor Ge-Ge distance is 0.242 nm. They also mentioned that Ge with

two dimensional honeycomb structure have novel physical properties akin to graphene such as the linear energy dispersion at the Fermi level[13]. The compatibility of germanene with semiconductor based nanotechnology will make this material particularly interesting for device applications.

However, germanene does not seem to exist in nature nor is there any solid phase of germanium similar to graphite. As a consequence, pure two dimensional germanene sheets cannot be generated by exfoliation methods as performed initially in the case of graphene. More sophisticated methods have to be considered for the growth or synthesis of germanene. One promising concept for synthesis of germanene is to deposit Ge on the metal surfaces that do not interact strongly with Ge atoms or form compounds. Recently, Ag(111) substrate had been used successfully for the synthesis of silicene[7-11]. Oughaddou et al. reported a ($\sqrt{3} \times \sqrt{3}$) $R30°$ structure as Ag_2Ge 2D surface alloy formation by Ge adsorption on Ag(111)[14]. But Kara et al. reported that the Ag-Ge surface alloy formation is quite unusual due to the large miscibility gap[15] in the bulk phase diagram. They also mention fcc(111) face has the chemical tendency to form the homo-atomic bonds rather than the surface alloy[15]. So that in order to grow real two-dimensional germanene sheets, Ag(111) surfaces, with sixfold top-layer symmetry, can be utilized, which might support the formation of a honeycomb Ge adlayer.

In this paper, we present an experimental study of the self-organized germanium superstructures on Ag(111), by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). We found that, depending on the germanium coverage several superstructures can be formed on Ag(111). We mentioned structural evolutions of germanium growth on Ag(111), which is desirable for fabrication of high-quality germanene and exploring its physics and applications. We proposed an atomic model for germanene grown on Ag(111) based on LEED and STM results.

2. Experimental

Experiments were performed in two ultrahigh vacuum (UHV) chambers, one equipped with a four grid LEED system and the other with STM. Clean and well-ordered Ag(111) surface was prepared by Ar-ion sputtering (1.0 kV, 1 μA, 30 min) and subsequent annealing at ≈ 760 K for 45 min under UHV condition. Ge was deposited by using a Ge source consisting of a directly heating Ge wafer piece, while the Ag(111) was kept at room temperature (RT). The temperatures of the substrate were measured by a thermocouple. After deposition, the sample was annealed at 415 K and we waited until the sample temperature became to RT again before starting LEED and STM measurements. In the STM chamber, the surface structure was characterized by LEED before STM observation. STM observations were performed at RT in a constant current mode using an UNISOKU RT-STM with a platinum-Iridium tip. WSxM 5.0 Develop 7.0 software was used for STM image processing[16].

3. Results and discussions

Figure 1 summarizes the obtained LEED patterns, showing the structural evolution for germanium growth on Ag(111) as a function of temperature and deposition time. We obtained a quasi ($\sqrt{3} \times \sqrt{3}$) R 30° pattern with broaden integer spots by 5 min Ge adsorption on Ag(111), while the substrate was at RT. The pattern became more intense with higher background at 9 min Ge deposition at RT [Fig. 1(a)]. After annealing the sample at 415 K, we got a $\left(9\sqrt{3} \times 9\sqrt{3}\right)R$ 30° pattern, as shown in Fig. 1(b). With increasing deposition time to 11 min and subsequent annealing at 415 K, we found rectangular c($\sqrt{3} \times 7$) pattern coexisting with $\left(9\sqrt{3} \times 9\sqrt{3}\right)R$ 30° pattern, depending on the sample position. With further increasing Ge adsorption on Ag(111) to 18 min and subsequent annealing at 415 K, we got a (12×12) pattern. We obtained only quasi ($\sqrt{3} \times \sqrt{3}$) R 30° structure with broaden integer spots for 5-18 min Ge adsorption on Ag(111) while keeping the sample at RT during deposition and no subsequent annealing of the sample after deposition. On contrast, by annealing the sample at 415 K after Ge adsorption on Ag(111), the quasi ($\sqrt{3} \times \sqrt{3}$) R 30° transferred to different phase for different adsorption time (as mention above). For the slower rate of Ge deposition on Ag(111), we obtained the $\left(9\sqrt{3} \times 9\sqrt{3}\right)R$ 30° pattern by 55 min Ge adsorption on Ag(111). In the case of the slower rate of deposition, a faint $\left(9\sqrt{3} \times 9\sqrt{3}\right)R$ 30° pattern was observed for Ge adsorption on Ag(111) while the sample was kept at RT and the pattern became clear after annealing the sample at 415 K.

Oughaddou et al. reported that the coverage of germanium of the rectangular c($\sqrt{3} \times 7$) superstructure for Ge adsorption on Ag(111) is one monolayer[17]. But their acquired LEED pattern has high background and showed a few numbers of spots for c($\sqrt{3} \times 7$)

superstructure. In our experiment, we obtained a clear LEED pattern with low background, fully accounting for the c($\sqrt{3} \times 7$) structure. Since we found the rectangular c($\sqrt{3} \times 7$) superstructure in coexistence with $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern, we consider that the germanium coverage for $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern is close to one monolayer. The $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern by germanium adsorption on Ag(111) is analogous to $(6\sqrt{3} \times 6\sqrt{3})R\,30°$ pattern of the graphene on SiC(0001)[18].

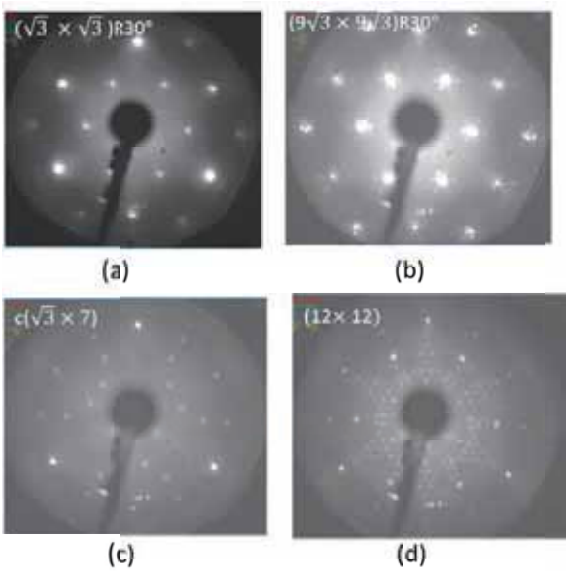

Fig. 1. LEED patterns for growth of Ge on Ag(111). (a) 9 min Ge adsorption at room temperature. (b) 9 min Ge adsorption at 415 K. (c) 11 min Ge adsorption at 415 K. (d) 18 min Ge adsorption at 415 K. All snaps were taken at the incident electron energy of 70 eV.

To have direct structural information about Ge/Ag(111), we have performed STM measurements. Figure 2 shows the atomically resolved STM images for monolayer Ge on Ag(111). Atomically resolved structures were observed for one monolayer Ge as shown in Fig. 2(a). Honeycomb structures were found on the STM image. The center to center distance between two nearest neighbor honeycomb [displayed as the black spots on Fig. 2(a)] was 0.45 $\pm$ 0.01 nm.

Oughaddou et al. reported a ($\sqrt{3} \times \sqrt{3}$) $R\,30°$ superstructure for Ge adsorption on Ag(111) and also suggested that the germanium atoms occupied the substitution sites on Ag(111) to form an ordered surface alloy. However, their observed atomically resolved STM image was quite similar to clean Ag(111) with no chemical contrast[14]. The surface alloy formation for Ge adsorption on Ag(111) is unlikely since the chemical tendency of the system prefers to phase separation, as the bulk phase diagram displays a large miscibility gap[15]. The observed ($\sqrt{3} \times \sqrt{3}$) $R\,30°$ structure appeared with broaden integer spots and it transferred to well ordered $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ moiré pattern after annealing at 415 K.

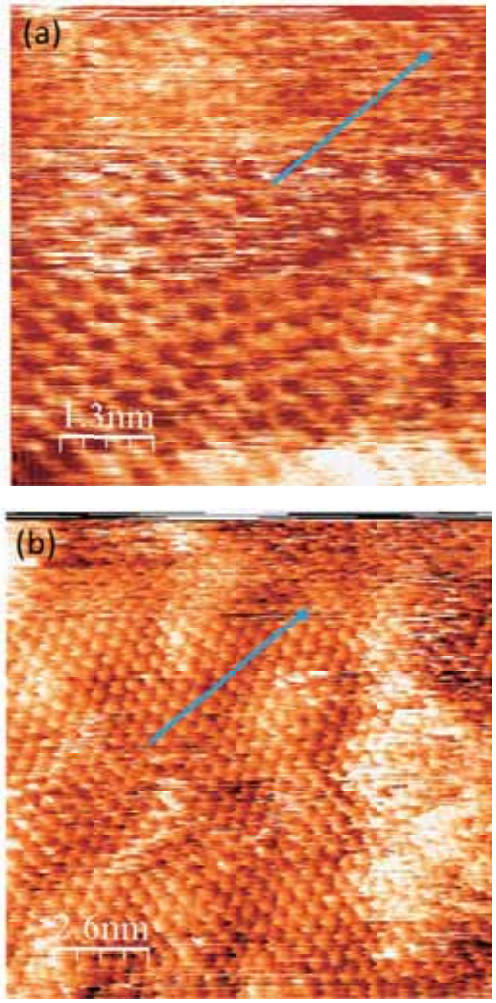

Fig. 2. Empty-state atomically resolved STM image after one monolayer germanium adsorption on Ag(111). The blue arrows indicate the [$1\bar{1}0$] direction of Ag(111) surface. (a) Scan area (6.5 nm × 6.5 nm) representing honeycomb lattice structure; V_{tip}= -0.1 V and I_{tip}= 3.0 nA. (b) Scan area (13 nm × 13 nm) representing $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ moiré structure; V_{tip}= -1.02 V and I_{tip}= 1.0 nA.

In another STM image of Fig. 2(b), protrusions with a long range order could be found, which might correspond to a moiré structure with the periodicity of $(9\sqrt{3} \times 9\sqrt{3})R\,30°$. From the moiré structure formation, this might state that the germanium atoms took place on the Ag(111) atoms (hollow, bridge and top sites) rather than taking substitution sites. Most probably in this case, germanium made a homo-atomic bonds in the overlayer.

Since the observed $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ pattern by LEED for germanium adsorption on Ag(111) is analogous to graphene formation on SiC(0001) and STM observation showed the honeycomb structure, we tentatively propose a model for germanene growth on Ag(111) based on the LEED and STM results.

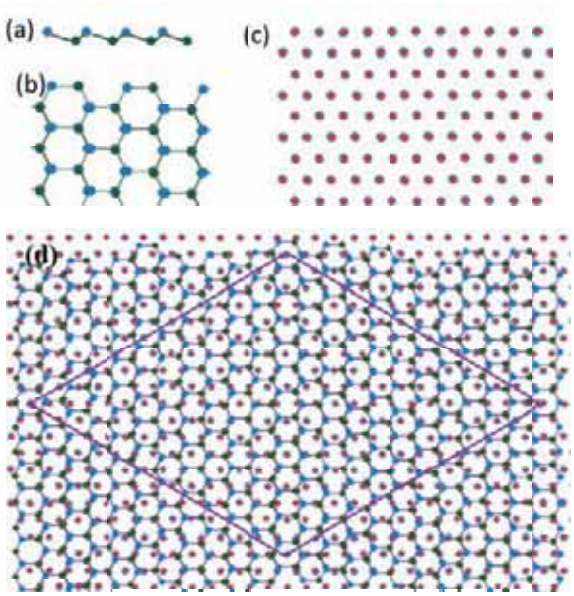

Fig. 3. Atomic model for germanene growth on Ag(111). (a), (b) The lattice geometry of germanene overlayer from the side and top views, respectively. (c) The lattice geometry of clean Ag(111) substrate. (d) $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ phase of germanene growth on Ag(111). The blue and green spots represent the upper and lower Ge atoms, respectively. The red spots represent Ag atoms. The rhombus represents the unit cell of the super structure.

Our germanene model is shown in Fig. 3. Figures 3(a) and 3(b) represent the side and top views of the germanene honeycomb lattice structure, respectively. The blue atoms would appear higher than the green atoms on Ag(111) surface due to the small buckling of the germanene structure. Figure 3(c) represents the lattice geometry of clean Ag(111) surface and Fig. 3(d) represents the model for germanene growth on Ag(111) surface, respectively. The nearest neighbor distance between the blue-atoms is about $\sqrt{3}$ times of the nearest neighbor Ge-Ge atoms distance in the germanene lattice. In our proposed model, the distance between the nearest neighbor Ge-Ge atoms (i.e the distance between nearest neighbor blue atom and green atom) is 0.254 nm, which is 5 % and 6.7 % larger than that of theoretically predicted by Liu et al.[13] and Cahangirov et al.[12], respectively.

4. Conclusion

In conclusion, the evolution of the germanium structure grown on Ag(111) substrate was investigated by LEED and STM. Various super structures of germanium were observed on Ag(111) using LEED, depending on the germanium coverage and the annealing temperatures. Among them, atomically resolved images were obtained for the one monolayer germanium adsorption, which corresponds to $(9\sqrt{3} \times 9\sqrt{3})R\,30°$ structure. The observed STM image showed a honeycomb structure, indicating the formation of germanene on Ag(111) in analogue to graphene. Based on the LEED and STM results, we proposed an atomic model for germanene on Ag(111).

References

1) A. K.Geim and K. S. Novoselov, *Nat. Mater.*, **6**, 183 (2007).

2) A.H. Castro Neto, F. Guinea, N.M.R. Peres, K. S. Novoselov, and A. K.Geim, *Rev. Mod. Phys.*, **81**, 109 (2009).

3) M. Pumera, *Chem. Rec.*, **9**, 211 (2009).

4) K.S. Kim, Y. Zhao, H. Jang, S. Y. LEE, J. M. Kim, K. S. Kim, J. –H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, *Nature*, **457**, 706 (2009).

5) B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara and S. Sebastien, *Appl. Phys. Lett.*, **97**, 223109 (2010).

6) K. Tadeka and K. Shiraishi, *Phys. Rev. B*, **50**, 14916 (1994).

7) G.G. Guzman-Verri and L.C. Lew Yan Voon, *Phys. Rev. B*, **76**, 14916 (2007).

8) B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Cheng, L. Chen, and K. Wu, *Nano Lett.*, **12**, 3507 (2012).

9) P. Vogt, P.D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio, A. Resta, B. Ealet and G.L.

Lay , *Phys. Rev. Lett.*, **108**, 155501 (2012).

10) H. Jamgotchain, Y. Colignon, N. Hamzaoui, B. Ealet, J.Y. Hoarau, B. Aufray and J. P. Biberian, *J. Phys.: Condens. Matter*, **24**, 172001 (2012).

11) R. Arafune, C.-L. Lin, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *Surf.Sci.*, **608**, 297 (2013).

12) S. Cahangirov, M. Topsakal, E. Akturk, H. Sahin and S. Ciraci, *Phys. Rev. Lett.*, **102**, 236804 (2009).

13) C.C. Liu, W.X. Feng, and Y.G. Yao, *Phys. Rev. Lett.*, **107**, 076802 (2011).

14) H. Oughaddou, S. Sawaya, J. Goniakowski, B. Aufray, G.L. Lay, J.M. Gay, G. Treglia and J.P. Biberian, *Phys. Rev. B*, **62**, 16653 (2000).

15) A. Kara, H. Enriquez, A. P. Seitsonen, L. C. L. Yan Voon, S. Vizzini, B. Aufray and H. Oughaddou, *Surf. Sci. Report*, **67**, 1 (2012).

16) I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, *Rev Sci. Instrum.*, **78**, 0.13705 (2007).

17) H. Oughaddou, S. Sawaya, J. Goniakowski, B. Aufray, G.L. Lay, J.M. Gay, G. Treglia and J.P. Biberian, *Phys. Rev. B*, **62**, 16653 (2000).

18) C. Riedl, U. Starke, J. Bernhardt, M. Franke and K. Heinz, *Phys. Rev. B*, **76**, 245406 (2007).