# Atomic Configuration of Germanene on an Al(111) Substrate Determined by using Total-Reflection High-Energy Positron Diffraction (TRHEPD)

We investigated the atomic configuration of germanene, a Ge counterpart of graphene, on an Al(111) substrate by using total-reflection high-energy positron diffraction (TRHEPD). The intensity analysis on the basis of dynamical diffraction theory showed that one Ge atom in the unit cell is shifted upwards, indicating an asymmetric structure. Our result is in sharp contrast to the previous structure model of a symmetric structure in which two Ge atoms are shifted upwards. However, the newly proposed structure does not contradict the experimental findings on electronic states in the previous studies.

Two-dimensional atomic sheets are attracting increasing research interest worldwide. A major type is graphene, a two-dimensional atomic sheet of carbon. Graphene with a honeycomb structure is attracting much attention because it has many promising characteristics such as extremely high carrier mobility, which stems from the unique electronic state of the so-called Dirac cone. Replacing carbon atoms by other group IV elements in the periodic table while keeping the honeycomb framework leads to the creation of novel two-dimensional functional materials. The Si and Ge counterparts of graphene are called silicene and germanene, respectively. In addition to high carrier mobility, these are predicted to have other fascinating properties such as quantum spin-Hall effect due to the expected buckled configurations from the strong $sp^3$ bonding character and the larger spin–orbit interaction in the relatively heavier atoms [1].

According to theoretical predictions [2], silicene and germanene have a buckled structure in the ground state. The electronic band structure strongly depends on the magnitude of the buckling [2]. However, since silicene and germanene do not exist in nature there has been no experimental investigation on the buckling. After pioneering works on the successful fabrication of silicene on a Ag(111) [3, 4] and $ZrB_2$ thin film [5] in 2012, silicene and germanene have been synthesized on various substrate surfaces. In 2013, we showed experimental evidence of the bucking configuration in silicene on a Ag(111) substrate [6].

In 2015, a uniform large-area germanene was successfully fabricated on an Al(111) substrate. Eight Ge atoms are included in the unit cell (see **Fig. 1**). In previous studies, it was suggested that two Ge atoms (labeled 2 and 7) in the unit cell are shifted upwards, leading to a symmetric structure (right of **Fig. 1**). However, the detailed atomic positions remained unknown. Thus, we tried to experimentally determine the atomic positions using total-reflection high-energy positron diffraction (TRHEPD) [7].

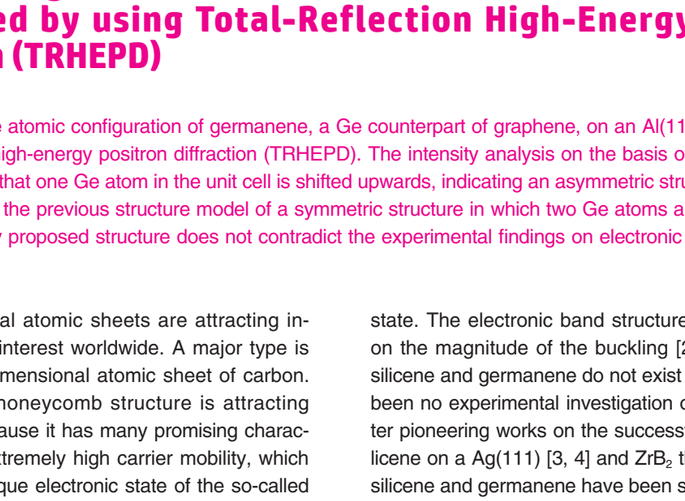


**Figure 1:** Atomic configuration of germanene on an Al(111) substrate determined in this study (left) and predicted in previous reports (right). Yellow and orange circles indicate the Ge atoms. Gray ones are the Al atoms. The unit cell is indicated by a light orange parallelogram. To highlight the bulked configuration, the Ge atoms shifted upwards are denoted by large yellow circles.

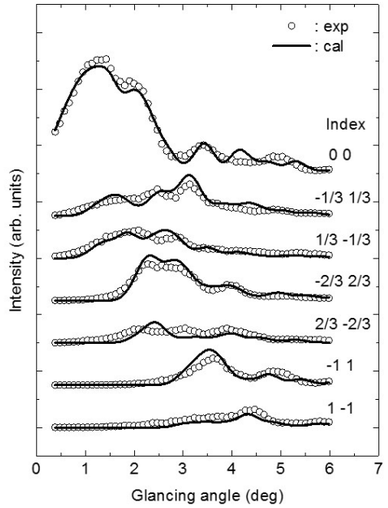


**Figure 2:** TRHEPD rocking curves for germanene on an Al(111) substrate. Open circles indicate the measured intensities. Solid lines are the intensities calculated using the optimum parameters.

TRHEPD is a surface-sensitive tool owing to the positive charge of the positron. The positron is the antiparticle of the electron and has the same mass and spin as the electron. Because the sign of the electric charge is opposite to that of the electron, the crystal potential for every material is positive. Thus, the refractive index for the positron is less than unity. This means that total reflection takes place at the material surface. For instance, the critical angle of the total reflection is estimated to be 2.0° using Snell's law when a positron beam with an energy of 10 keV is incident on a Si surface. Under the total reflection condition, the penetration depth of the positron beam reaches 0.5–1.0 Å, which corresponds to the thickness of one atomic layer. Therefore, the TRHEPD technique is suitable for determining the structure of two-dimensional atomic sheets suspended on particular substrates. TRHEPD apparatus combined with an electron linear accelerator was constructed jointly by JAEA and KEK.

As a result, we found that germanene on an Al(111) substrate has an asymmetric structure (left of **Fig. 1**), which is in sharp contrast to the symmetric one in previous reports [8]. We measured the rocking curves (TRHEPD intensity versus glancing angle) at a symmetric azimuth (**Fig. 2**). The intensity distributions of the equivalent diffraction spots, e.g., –1/3 1/3 and 1/3 –1/3 spots in **Fig. 2**, exhibit different shapes. Assuming the symmetric structure as reported in previous studies, the intensity distributions should show the same shape. Intensity analysis based on the dynamical diffraction theory confirmed that one Ge atom (labeled 7) in the unit cell is shifted upwards, giving rise to an asymmetric structure [7]. The newly proposed structure will help clarify the property of germanene on an Al(111) substrate.

## REFERENCES

[1] C. -C. Liu, W. Feng and Y. Yao, *Phys. Rev. Lett.* **107**, 076802 (2011).
[2] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin and S. Ciraci, *Phys. Rev. Lett.* **102**, 236804 (2009).
[3] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. Le Lay, *Phys. Rev. Lett.* **108**, 155501 (2012).
[4] C. -L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *Appl. Phys. Express* **5**, 045802 (2012).
[5] A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang and Y. Yamada-Takamura, *Phys. Rev. Lett.* **108**, 245501 (2012).
[6] Y. Fukaya, I. Mochizuki, M. Maekawa, K. Wada, T. Hyodo, I. Matsuda and A. Kawasuso, *Phys. Rev. B* **88**, 205413 (2013).
[7] Y. Fukaya, I. Matsuda, B. Feng, I. Mochizuki, T. Hyodo and S. Shamoto, *2D Mater.* **3**, 035019 (2016).
[8] M. Derivaz, D. Dentel, R. Stephan, M. -C. Hanf, A. Mehdaoui, P. Sonnet and C. Pirri, *Nano Lett.* **15**, 2510 (2015).

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