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研究課題名（和文）Germanene on Insulators: Towards the realization of a 2D topological insulator

研究課題名（英文）Germanene on Insulators: Towards the realization of a 2D topological insulator

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研究成果の概要（和文）：基礎科学分野において，また，様々な応用へ向けて期待が高まるゲルマニウムでできた二次元材料の形成，特に，グラフェン様の蜂の巣格子を持つゲルマネンの形成を主な目的とした．二ホウ化ジルコニウム薄膜上に自発形成される二次元状 Geの構造は二つの三角格子からなり，この構造は電子状態にフラットバンドを持つことが明らかとなった．また，二ホウ化ジルコニウム薄膜上シリセンにGeを蒸着して二次元SiGe混合層を形成し，バンド幅の制御を実験的に可能にした．その他，ゲルマネンとの格子整合性に優れ，電子状態への影響が少ないことが期待される基板としてInSeに着目し，Ge単結晶上への単結晶配向薄膜の成長に成功した．

研究成果の学術的意義や社会的意義
This project contributed to the development of two-dimensional materials which are of great interest for both applications and fundamental science as they possess novel properties and are solutions to scale down the dimensions of electronics components without increasing the heat dissipation.

研究成果の概要（英文）：This project was dedicated to the fabrication and the study of two-dimensional materials made of germanium and having a high potential for various applications and fundamental science. Its main objective was the realization of germanene, a graphene-like honeycomb lattice. Among the Ge structures we investigated, a single Ge layer spontaneously forming on ZrB2 thin films was identified as a bi-triangular lattice. This Ge structure features a flat band in its band structure from which exotic properties are predicted to emerge. We also demonstrated the feasibility of a band structure engineering in two-dimensional SiGe alloys verified experimentally in the one we fabricated by depositing Ge atoms on silicene on ZrB2. The project also addressed the preparation of ideal substrates for the growth of germanene. Good quality (0001)-oriented InSe thin films were successfully grown on Ge(111), which may allow for the lattice-matching Van der Waals growth of free-standing-like germanene.

研究分野：総合理工

キーワード：2D materials　germanium

１．研究開始当初の背景

Owing to their ultimate smoothness, flexibility, high surface sensitivity and the novelty of their properties, two-dimensional (2D) materials are of great interest for various applications in nanoelectronics. The merit of 2D materials is exemplified by the properties predicted for germanene, a graphene-like 2D material consisting of a buckled honeycomb lattice made of Ge atoms. As other 2D materials made of elements belonging to the group-14 of the periodic table (C, Si, Sn, Pb...), the calculated band structure of free-standing germanene features Dirac cones [1] which confer a massless-like character and very high mobilities to the charge carriers. Nevertheless, these 2D materials are predicted to be topological insulators [2], a class of materials insulating in the bulk but having edges featuring spin-polarized counter-propagating ballistic channels. Owing to their buckled structures, the existence of the edges states in germanene is predicted to be controllable by a vertical electric field, giving rise to switchable ballistic spin-currents.

All the above mentioned appealing properties are for the virtual free-standing forms of germanene, which so far do not exist. The formation of germanene by deposition of germanium on substrates like Pt(111) [3], Al(111) [4], Au(111) [5], MoS_2 [6] and graphite [7] was recently claimed by different groups in Europe and China but the predicted peculiar conduction properties were not measured.

２．研究の目的

The purpose of this project was to address the fabrication and the study of 2D structures made of Ge atoms. Its main objective was to realize a single layer of germanium with properties approaching those of free-standing germanene. For this purpose, single layers of Ge were planed to be grown on insulating or semiconducting substrates with weakly interacting surfaces such as h-BN-buffered ZrB_2 thin films we can fabricate in our laboratory and InSe thin films, whose growth on Ge(111) was part of the project. The study of the encapsulation of these 2D Ge layers by insulating materials, which is required to prevent their degradation in air, was postponed in order to give priority to the study of two other 2D Ge-rich structures we observed experimentally. (i) We could demonstrate that the surface of zirconium diboride (ZrB_2) thin films grown on Ge(111) is covered by a Ge-rich monolayer in a manner reminiscent of the spontaneous formation of silicene, a graphene-like form of silicon, on ZrB_2 thin films grown on Si(111). (ii) The deposition of germanium on silicene on ZrB_2 was found to result at low coverage to the formation of a silicene-Ge alloy.

３．研究の方法

(1) Samples

ZrB_2(0001) thin films were grown on Si(111) and Ge(111) by chemical vapor epitaxy in ultra high vacuum (UHV). The samples can then be transferred to any UHV system. The spontaneous and self-terminating formation of silicene on ZrB_2 thin films grown on Si(111) resulting from the segregation of Si atoms from the substrate, is induced by annealing the samples in UHV [8] A Ge monolayer can be generated in a similar manner on ZrB_2 thin films grown on Ge(111). ZrB_2 thin film grown on Si(111) buffered by a good quality h-BN single layer were obtained by nitridating the silicene layer by means of a N plasma and by a subsequent annealing. Ge depositions in UHV were realized by evaporating Ge in a K-cell. The growth of InSe on Ge(111) was performed in a molecular beam epitaxy (MBE) system equipped with standard thermal effusion cells used to evaporate simultaneously In and Se.

(2) Characterization techniques

The surface structures of the substrates and of 2D Ge structures were characterized in situ by means of several techniques including scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Ex-situ characterizations by atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM) were also conducted.

Density functional theory (DFT) calculations were performed to give support to the experimental findings. DFT calculations were carried out within a generalized gradient approximation (GGA) using the OPENMX code [9] based on norm-conserving pseudopotentials generated with multireference energies and optimized pseudoatomic basis functions.

４．研究成果

(1)Flat band in bi-triangular Ge structure on ZrB_2(0001)

The investigation of the Ge-rich structure spontaneously forming on ZrB_2(0001) thin film grown on Ge(111) by means of experimental techniques and DFT calculations were the object of a collaboration with different groups of the University of Tokyo and the Japan Atomic energy Agency. The Ge-rich layer appears in STM images as a ZrB_2(0001)-($\sqrt{3}\times\sqrt{3}$) reconstruction and was identified by means of reflection high energy positron diffraction and DFT calculations as a bi-triangular structure consisting of a (1×1) array of Ge atoms sitting on hollow sites of the Zr-terminated ZrB_2(0001) surface and of a ($\sqrt{3}\times\sqrt{3}$) array of Ge atoms protruding above Zr atoms. The analysis of the band structure of this Ge bi-triangular structure by ab-initio calculations suggests the existence of a 'flat band' i.e. a band showing almost no dispersion in the reciprocal space and from which, various exotic quantum phases are predicted to emerge.

In contrast to the case of intrinsically frustrated structures such as the Kagome lattice, tight-binding model of the Ge bi-triangular structure predicts the existence of a flat band for a specific ratio between the hopping integrals of the hopping between first neighbor bottom atoms and that of the hopping between a top atom and its first-neighbor atoms. DFT calculations showed that this condition is almost verified by the bi-triangular structure observed experimentally. This was verified by the experimental observation of the flat band in ARPES spectra which shows a small dispersion due to the interaction with the substrate. The fact that the flat band emerges from a specific ratio of hopping integrals, suggests that it can be tuned by modifying the Ge structure, for instance by the adsorption of adatoms.

(2) Band engineering in silicene-Ge alloy on ZrB_2(0001)

Alloys are materials of great interest for various technological applications ranging from electronics to metallurgy. This is exemplified by the engineering of the bandgap in semiconducting alloys which can be tuned with the ratio of their constituents.

The structure of epitaxial silicene sheet that forms spontaneously on top of ZrB_2 thin films grown on Si(111) (shown in the inset of Fig. 1.(a) and in Fig. 1.(c)), adopts a ($\sqrt{3}\times\sqrt{3}$)-reconstructed structure fitting with the (2×2) unitcell of ZrB_2(0001). In this unitcell, 5 atoms are laying in a same plane and a single atoms is protruding above a Zr atom. The deviation of this structure from that of free-standing silicene opens a gap in the Dirac cones centered on the *K* point of the Brillouin zone.

The possibility of forming a silicene-Ge alloy by depositing Ge on silicene was suggested by preliminary experiments. The evolution of the silicene structure upon deposition of Ge atoms in the 0-0.2 monolayer (ML) range was thoroughly investigated by STM, photoemission spectroscopy and DFT calculations. In STM images (Fig. 1.(a)), it appears that the deposition of Ge atoms preserves the ($\sqrt{3}\times\sqrt{3}$)-reconstruction of silicene but a contrast between protrusions is now visible. This is explained by the substitution of Si atoms occupying the protruding sites by Ge atoms. The core-level spectrum of

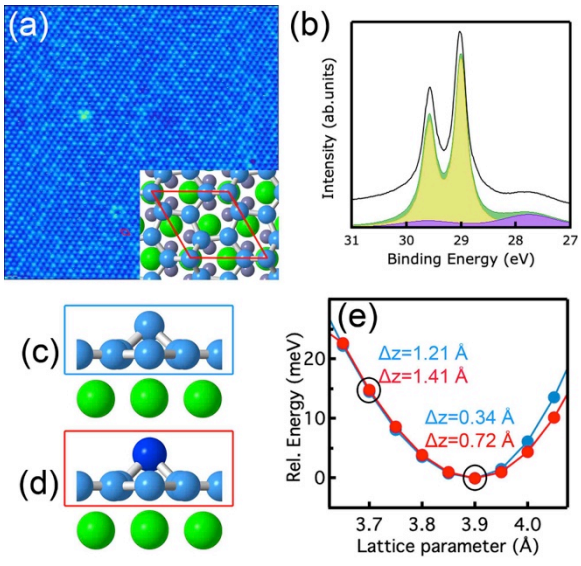

Figure 1. (a): STM image after deposition of 0.06 ML Ge on silicene. The inset shows a top view of the silicene structure determined from DFT calculations. The ($\sqrt{3}\times\sqrt{3}$) unitcell is indicated by a red rhombus. (b): Core-level spectrum recorded after deposition of 0.09 ML Ge. The yellow and purple filled curves correspond to fitted Ge3d and Zr4p doublets. (c) and (d): Side views of the structures of silicene and Si_5Ge on ZrB_2(0001) determined from DFT calculations. Light blue-, dark blue- and green-colored atoms are Si, Ge and Zr atoms respectively. (e): Lattice parameter-dependence of the energy of silicene and Si_5Ge planar-like free-standing structures. The height differences between bottom and top atoms for the lattice parameters corresponding to the minimum of the curves and to the epitaxial conditions, are indicated.

Fig. 1.(b) features a single Ge3d doublet, which indicates that Ge atoms occupy solely the protruding sites. For a Ge coverage corresponding to 1/6 ML (i.e. the density of protruding atoms in epitaxial silicene) a Si_5Ge compound is realized (Fig. 1.(d)). The characterization of the band structure around the *K* point of the silicene-Ge alloy for different Ge coverages (Fig. 2) shows that the top of the valence band varies monotonously from 460 meV (Fig. 2.(a)) for silicene to 310 meV (Fig. 2.(b)) for Si_5Ge, which provides the first experimental demonstration of an electronic band structure engineering in 2D SiGe alloy by means of the concentration of Ge atoms. DFT calculations indicate that in their free-standing forms, silicene and Si_5Ge would adopt the same lattice parameter (Fig. 1.(e)). This suggests that the influence of the Ge atoms does not result from a change in the epitaxial strain.

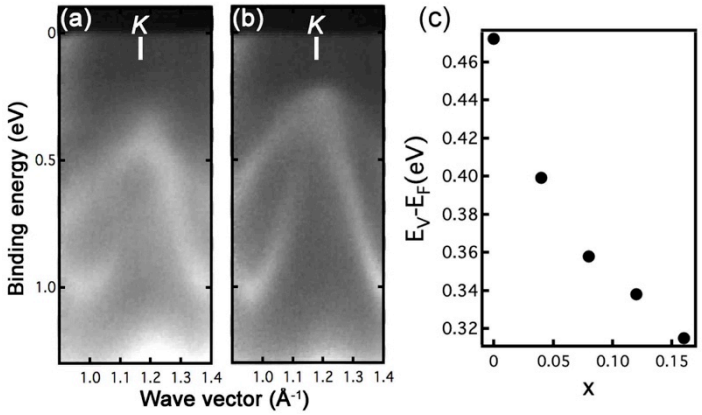

Figure 2. (a) and (b): ARPES spectra recorded around the K point of the Brillouin zone for silicene and Si_5Ge. (c): Evolution of the valence energy E_V with respect to the Fermi level E_F.

(3) Deposition of germanium on h-BN/ZrB_2(0001)

In contrast to the deposition of silicon on h-BN/ZrB_2 which gives rise to intercalated silicene [10], LEED pattern suggests that the deposition at room temperature of germanium on h-BN/ZrB_2 leads to an amorphous layer. The h-BN-related spots tend to disappears upon post-deposition annealing. The typical LEED pattern of epitaxial silicene on ZrB_2(0001) appears instead, which suggests that the deposition of Ge induces the vanishing of the h-BN layer. It is thus suggested that h-BN is not a suitable substrate for the growth of germanene.

(4) InSe thin films on Ge(111)

InSe is an ideal semiconducting template for the lattice-matching Van der Waals growth of germanene: InSe is a III-VI chalcogenide with a layered structure along its [0001] direction and its (0001) surface lattice parameter (4.02 Å) is very close to that predicted for free-standing germanene.

The possibility of growing InSe thin films on Ge(111) was verified experimentally. Crystalline thin films were obtained for growth temperature of 400ºC. The thin films grow with the c-axis parallel to Ge(111). The thin films appear on AFM images recorded in tapping mode as triangular pyramid-like hills consisting of atomically flat terraces separated by single steps (Fig. 3.(a)). The crystallographic structure resolved by means of cross-sectional high-angle annular dark field STEM (HAADF-STEM) in collaboration with the group of Prof. Oshima of JAIST, consists mostly of a ε-type stacking of InSe layers separated by Van der Waals gaps (Fig. 3.(b)). Most of the single layers adopt a prismatic structure (in which top and bottom Se atoms are on top of each others) but antiprismatic layers are also found locally. Nevertheless, we could demonstrate that the InSe thin film surface can be flattened by using the scotch tape technique. The so-obtained flat and homogeneous InSe(0001) surface offers a perfect template for the growth of germanene whose study will be investigated in the continuation of this project.

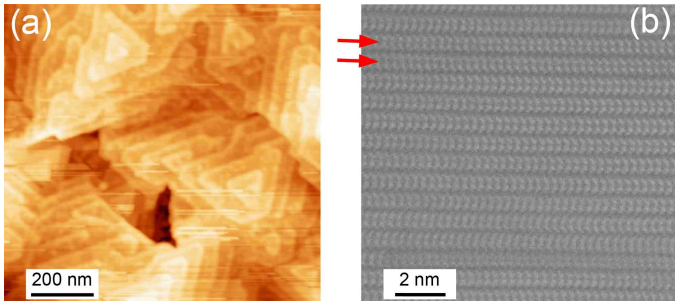

Figure 3. (a): Air-AFM image recorded in tapping mode on as grown InSe thin film grown on Ge(111). HAADTF-STEM image. The red arrows indicate antiprismatic layers

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