Evolution of the structural and electronic properties of thin Bi films on Ge(111)

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Evolution of the structural and electronic properties of thin Bi films on Ge(111)

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Abstract. We have incrementally grown bismuth thin films onto a n-doped Ge(111) substrate. Low energy electron diffraction reveals that the first Bi atomic layer is characterized by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction. By angle-resolved photoemission spectroscopy we observe Rashba-split bands that do not cross the Fermi level. At higher coverages, where a Rashba type of splitting should still be present, the density of occupied states close to the Fermi energy gradually increases, while extra diffraction spots, related to Bi(110) islands, appear.

1. Introduction

Electrons in bismuth, thanks to its high atomic number ($Z_{\mathrm{Bi}} = 83$), are subject to a huge spin-orbit interaction. This makes Bi one of the most appealing materials for spintronic applications. Despite bulk Bi is a non-magnetic material and a semimetal, in reduced-symmetry environments its electronic structure can be dramatically changed and its spin-related properties boosted. For instance, in Bi thin films it is possible to induce a transition into a semiconductor as a function of thickness [1, 2] or into a semiconductor or a topological semimetal as a function of strain [3]. Furthermore, confinement promotes the formation of quantum well-related states [4, 5], while the removal of inversion symmetry at surfaces or interfaces yields a non null Rashba term in the hamiltonian, resulting in spin-polarized surface bands [6–9].

In this context, particularly important for both fundamental and technological reasons is the deposition of Bi films onto semiconductors. Noteworthy, the Rashba effect is found to be greatly enhanced in one monolayer (ML) of Bi deposited on Ge(111) [7, 8] with respect to the (111) surface of bulk Bi [10]. This highlights the active role played by the substrate and calls for a more detailed study of the interplay between the two media. Moreover, Ge is one of the key semiconductor for spintronic applications [11–13], due to inversion symmetry, absent in III-V semiconductors [14, 15], which results in long electron spin lifetime. In this work we present an analysis of the structural and electronic properties of ultrathin Bi layers grown on n-doped Ge(111), based on X ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and angle-resolved photoemission (ARPES).

2. Materials and methods

A Sb-doped Ge(111) substrate ($N_{\mathrm{D}} = 1.1 \times 10^{16}$ cm^{-3}) was cleaned by cycles of Ar^+ sputtering (1 kV, normal incidence) and thermal annealing (1175 K for few minutes) until a sharp $c\,(2 \times 8)$

reconstruction was visible at LEED [7, 17, 18]. Bismuth was then evaporated from a boron nitride crucible at a rate of about 1 Å/min, calibrated by a quartz microbalance. The base pressure was in the low 10^{-8} Pa. As a standard procedure [8], the first Bi single layer was obtained by room temperature deposition of an amount of Bi slightly above 1 ML.[1] The excess material was then removed by heating the sample for 5 min at 725 K [8]. Further Bi layers were grown by depositing the exact quantity at room temperature without annealing.

XPS and ARPES measurements were performed by illuminating the sample with unmonochromatized Al Kα radiation ($h\nu$ = 1486.6 eV) and unpolarized He Iα radiation ($h\nu$ = 21.2 eV), respectively. Photoelectrons were collected by a 150 mm hemispherical analyzer (from SPECS GmbH) equipped with a standard multichannel detector, operating with a pass energy of 0.5 eV (20 eV) and providing a full width at half maximum resolution of 40 meV (0.9 eV) for ARPES (XPS) [19]. Wave-vector selection was obtained by tilting the sample around the [11$\bar{2}$] direction [see Fig. 1(d)], whereas Fermi level (ε_F) was determined from the metallic Fermi edge of a Ta foil. All measurements were performed with the sample at 100 K.

3. Structural evolution

The LEED measured on 1 ML Bi/Ge(111) [Fig. 1(a)] shows both the (1×1) pattern related to the germanium substrate (red dashed line) and the $(\sqrt{3} \times \sqrt{3})R30°$ [from now on: $(\sqrt{3} \times \sqrt{3})$] reconstruction (green dashed line) typical of the bismuth first layer, which is known to form

[1] Bismuth monolayer thickness (2.55 Å) is the deposed bismuth quantity which matches the atomic density of Ge(111) surface, *i.e.* $7.21 \cdot 10^{14}$ atoms/cm^2.

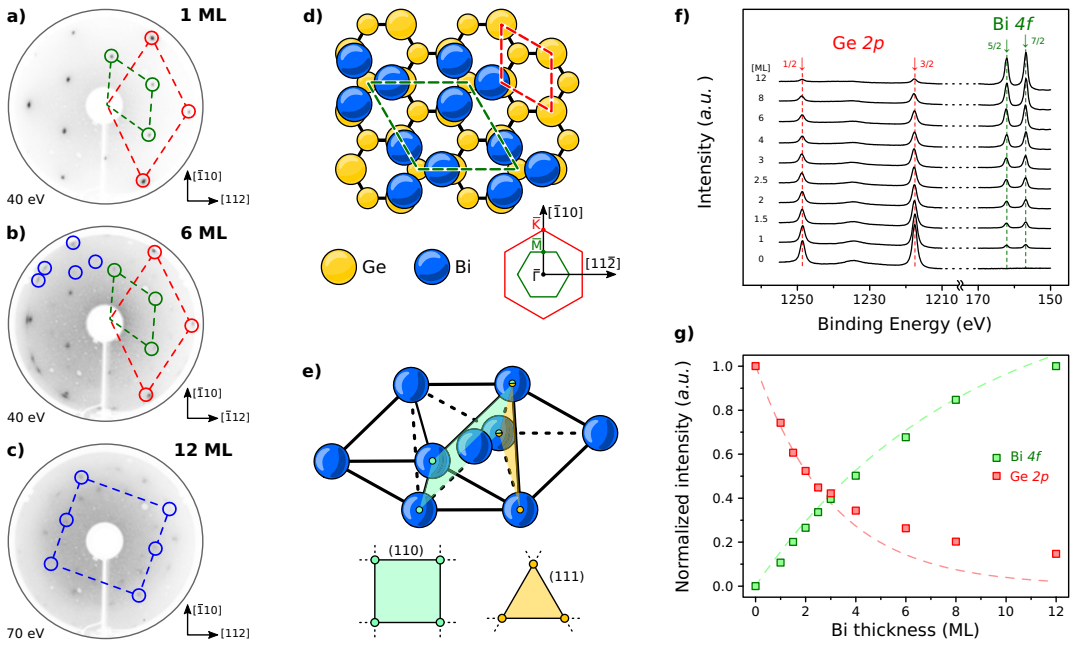

Figure 1. (a-c) LEED spectra of 1, 6 and 12 ML of Bi/Ge(111). Green [red] dashed lines show the unit cell of the Ge(111) surface [$(\sqrt{3} \times \sqrt{3})$ reconstruction], while blue ones are related to the (1×1) pattern of Bi(110). (d) Real lattice configuration of the first Bi layer, with a sketch of the (1×1) and $(\sqrt{3} \times \sqrt{3})$ surface first Brillouin zone. (e) Bulk Bi unit cell in which the pseudosquare (110) and hexagonal (111) planes are highlighted, reported underneath as top views. (f) Bi 4f and Ge 2p XPS spectra and (g) peak intensities vs. Bi coverage (lines: exponential fits performed with inelastic mean free paths consistent with Ref. [16]).

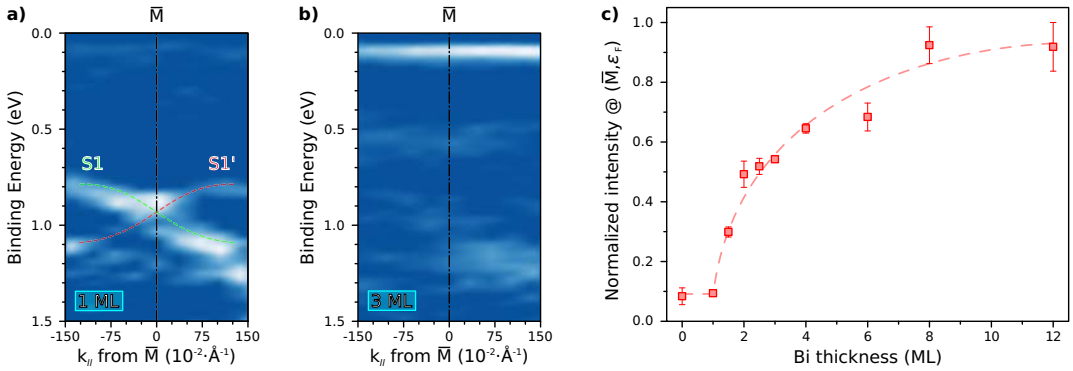

Figure 2. (a,b) Valence band map – obtained as in Ref. [8] – along the $\overline{\Gamma K}$ direction around the $\overline{\mathrm{M}}$ point of the $(\sqrt{3}\times\sqrt{3})$ SBZ of 1 and 3 ML Bi/Ge(111). (c) Intensity of ARPES spectra measured at ε_{F} as a function of the Bi thickness, probed at the $\overline{\mathrm{M}}$ point of the $(\sqrt{3}\times\sqrt{3})$ SBZ.

trimers with both Ge(111) and Si(111) substrates [20, 21]. The corresponding direct-space lattice is shown in Fig. 1(d) with the same color convention. For a thickness $\geq$ 2 ML, weak LEED spots appear [blue circles in Fig. 1(b) for 6 ML], with increasing intensity at higher coverages, forming a fully-developed (1×1) reconstruction around 12 ML [Fig. 1(c)]. According to the STM analysis by Hatta *et al.* [20], such spots are indicative of the presence of pseudosquare Bi(110) islands [see Fig. 1(e)]. It is worth noticing that the stability of these islands, as recently pointed out in other ultrathin films [22, 23], is driven by the epitaxy with the substrate, since, for higher coverages Bi thin films on Ge shows the (111) surface [20]. Notably, the 6 ML pattern partially retains the hexagonal Bi reconstruction, whereas at 12 ML it is barely visible.

XPS spectra [Fig. 1(f)] show the decrease (increase) of Ge $2p$ (Bi $4f$) peak with increasing Bi coverage, as reported in Fig. 1(g). It is worth mentioning that the Ge $2p$ intensity deviates from the exponential attenuation curve above $\approx$ 4 ML, as expected in the case of island nucleation [24, 25]. In this case, in fact, the signal from the substrate is less quenched than in a layer-by-layer growth, since regions not covered by islands provide a signal that reaches a non vanishing saturation value [26]. Notably, Bi $4f$ peak intensity does not show the same deviation from the exponential curve because the inelastic mean free path (IMFP) of Bi $4f$ electrons ($\approx$ 11 ML) is three times larger than the one of Ge $2p$ electrons [16], making the former less sensitive to the overlayer inhomogeneities. Similarly, Ge $2p$ IMFP limits XPS sensitivity, so that 4 ML have to be considered as an upper bound of island nucleation starting coverage, in agreement with the 2 ML revealed at LEED. Hence, XPS and LEED analysis suggest a Stranski-Krastanov growth mode for this system, with the formation of a single $(\sqrt{3}\times\sqrt{3})$ wetting layer and Bi(110) islands. Very recent STM data seems to support this interpretation.

4. Electronic structure

As reported in our previous work [7], for the single layer we observe a strong Rashba splitting of Bi surface resonance band, resulting in two spin-polarized branches [S1 and S1' in Fig. 2(a)] symmetric with respect to the $\overline{\mathrm{M}}$ point of the $(\sqrt{3}\times\sqrt{3})$ surface first Brillouin zone (SBZ), and located at around 1 eV below ε_{F}. In this case, no band is observed to cross ε_{F}, in agreement with Sandomirskii's prediction [27], according to which bismuth should maintain a semiconductor-like character up to a critical thickness, later estimated to be about 100 ML [28]. Nevertheless, as reported in Fig. 2(b), the second derivative of the experimental spectra measured for 3 ML clearly indicates the presence of states close to ε_{F}. This is in qualitative agreement with both experiments [in Bi/Si(111) films thicker than 10 ML] [4] and *ab initio* calculations [thin Bi(110)

films] [1], which contradict the prediction of Ref. [28]. To study the density of states (DOS) at ε_F as a function of the coverage we have normalized the acquired spectra to the same background value at a binding energy of 5 eV, where no spectral feature is observed. It can be noticed that the DOS, evaluated at $\overline{M}$, begins to increase for a Bi thickness just larger than 1 ML [Fig. 2(c)]. Notably, according to Refs. [1] and [9], the Rashba effect should be significant also for these coverages, *i.e.* for bands crossing ε_F, paving the way to potential applications in spintronics.

5. Conclusions

We have studied ultrathin Bi/Ge(111) films as a function of the Bi coverage. Bi atoms in the 1 ML-thick film are arranged in trimers while the film itself has a semiconducting character. At higher thickness we measured a nonvanishing DOS at the Fermi level, together with the observation of a Bi(110) island nucleation. Notably, the Rashba splitting should be present also for high coverages, making the states crossing the Fermi level spin-polarized.

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