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Tailoring the electronic structure of thin Bi films via the growth on vicinal Ge(111)

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ABSTRACT

The realization of a regular distribution of defects or step edges with a specific orientation at the surface of a semiconductor or a semimetal, such as Bi, might have interesting implications for both fundamental studies and applications, due to the electronic properties stemming from their peculiar topology. Here we present an accurate comparison of the morphological and electronic structure of thin Bi film (with a thickness of 10 nm) grown on Ge(111) and on a high index Ge(111) vicinal surface, Ge(223). We make use of low energy electron diffraction (LEED) and spin-resolved photoemission spectroscopy (SR-PES) for the crystallographic and electronic characterization, respectively. We show that on both substrates it is possible to grow thin Bi films showing the hexagonal Bi(111) surface orientation, whose spin-resolved electronic structure is reminiscent of the one characteristic of bulk Bi(111). At variance with the films grown on Ge(111), those grown on Ge(223) present some specific features, namely the presence of a splitting in the LEED diffraction spots and a reduced momentum dispersion of the electronic states. We interpret these features as evidences that the peculiar morphology of the substrate can be indeed used to modulate the growth of the Bi film leading to the formation of a stepped Bi surface.

Keywords: Bismuth, Ge(111), vicinal surface, LEED, spin-resolved photoemission

1. INTRODUCTION

Bismuth is a prototypical group V semimetal characterized by peculiar electronic structure featuring a narrow Fermi surface.[1] The low density of charge carries makes its electrical, crystallographic and electronic properties closely intertwined and particularly sensitive to external perturbations such as temperature variations or applied stresses.[2–4] Unlike other *sp* bonded materials, notably group IV semiconductors, Bi is characterized by the presence of metallic surface states, strongly contributing to the electronic properties of the material.[5] In addition, as a consequence of its large atomic number, the spin-orbit interaction plays a relevant role in determining the Bi electronic band structure. For instance, surface electronic states are split in spin-polarized bands by the so-called Rashba effect,[6,7] an occurrence that can be exploited in the field of spintronics for, *e.g.*, the generation and manipulation of spin currents.[8–10]

For such technological applications, Bi is employed in the form of thin films or nanostructures. This results in a complex scenario where different phenomena have to be accounted for: (i) the interaction with the substrate leading, for instance, to the occurrence of metastable/allotropic phases;[11–13] (ii) confinement effects become relevant, thanks to the considerably larger De Broglie wavelength and mean free path of carriers in Bi with respect to traditional metals;[14–16] (iii) the surface electronic structure is modified by the presence of defect or edge states, depending on the film morphology.[17,18] All these occurrences have been highlighted in a number of studies performed on thin Bi films, from single layers to nanometer thick films, grown on technologically relevant substrates such as, *e.g.*, Si, Ge or GaAs.[13,19–22]

The (111) face of Si and Ge guarantees the growth of high quality Bi films, which proceeds via the formation and successive coalescence of islands with a crystallographic structure reminiscent of the rhombohedral lattice of bulk Bi, which can be viewed as a stack of buckled bilayers (BL), with one bilayer weakly bonded to the adjacent ones along the [111] direction.[6] The exact crystallographic evolution of Bi films is rather complex and influenced by several factors, including the substrate temperature and the actual atomic arrangement at the Bi/semiconductor interface.[11,23] Generally, at low coverages a Bi(110)-like, or "pseudocubic" face is usually observed, while at larger Bi coverages an "hexagonal" Bi(111) face is stabilized.[13,19,20,24] Given the theoretical prediction of non-trivial topological properties of a system of Bi BL, and hence the possible presence of topologically protected boundary states, the Bi(111) surface has been extensively

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investigated.[18,25,26] In Ref. 27, a bulk Bi crystal showing a Bi(114) surface, with a substantially high miscut angle with respect to the parent (111) plane, has been employed to highlight the properties of the Bi BL edge states. Other attempts to realize a vicinal Bi(111) surface on thin films exploiting a high-index vicinal substrate, such as Si(553), highlighted the possible drawback constituted by the poor stability of the substrate against faceting, and its contribution to the nucleation of Bi islands with a different orientation.[28,29]

In the present work, we investigate the growth of 10 nm thick Bi films on Ge(111) and Ge(223) by means of low energy electron diffraction (LEED) and spin-resolved photoemission spectroscopy (SR-PES). Our results show that in both cases, the typical signatures of the hexagonal Bi(111) surface are observed. In addition, on the thick Bi film grown on Ge(223), the splitting of the LEED diffraction spots in the direction perpendicular to the substrate's step edges suggests the stabilization of a stepped Bi(111) surface, a promising result in view of a more detailed analysis of the contribution of edge states to the surface electronic structure.

2. MATERIALS AND METHODS

The growth and characterization of the Bi films was performed in a custom made ultra-high vacuum system operating at a base pressure of 10^{-11} Torr and described with more details in Ref. 30. The Ge(111) and Ge(223) substrates (Sb-doped, resistivity ρ=0.18 Ω·cm) were cleaned by repeated cycles of Ar ion sputtering (E_{Ar}=1 keV) and annealing at 1100 K until a sharp LEED pattern was observed. Care was taken to ensure a low cooling rate (about 50 K per minute) from high temperature to promote the long range ordering of the surface.[31] Bi films with a thickness of 10 nm were produced by evaporating Bi from a thermally heated boron nitride crucible onto the substrate kept at room temperature. The Bi flux was calibrated by means of a quartz microbalance and was maintained at about 1-2 Å/min. In order to improve the quality of the deposited film, samples were post-annealed for a few minutes at about 400 K.[20] SR-PES measurements were performed *in-situ* in a separate chamber equipped with a source of unpolarized HeI radiation ($hv = 21.22$ eV) and an hemispherical electron analyzer coupled to a Mott detector.[30] The energy- and angular- full width at half maximum (FWHM) resolution of the analyzer were set at about 100 meV and 2°, respectively. During the SR-PES measurements, the sample temperature was kept at 100 K by means of a closed-cycle He cryostat.

3. RESULTS AND DISCUSSION

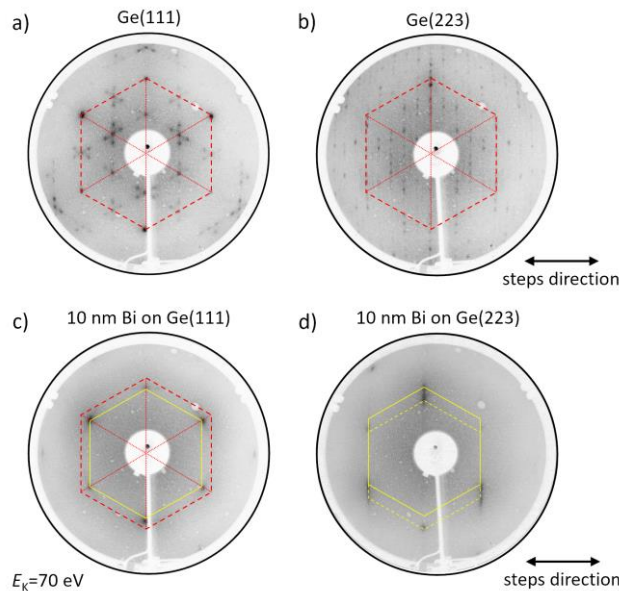The LEED characterization of the Ge(111) and Ge(223) substrates is shown in Figure 1a,b.

Figure 1. LEED pictures recorded on a,b) the Ge(111) and Ge(223) substrates and c,d) after the growth of a 10 nm thick Bi film at an electron beam energy of 70 eV. The substrates were aligned in order to impinge with the electrons roughly along the $[111]_{Ge}$ direction. Red (yellow) lines highlight the hexagonal diffraction pattern related to the (111) surface of Ge (Bi). Step edges (horizontal lines) extend along the $[\bar{1}10]_{Ge}$ direction.

The Ge(111) diffraction pattern of Figure 1a shows the well-known c(2×8) superstructure, indicative of the formation of a high quality surface.[32] No contaminants were detected by a complementary characterization performed with X-ray photoemission spectroscopy (data not shown). In a truncated-bulk picture, the Ge(223) surface consists in monoatomic $(111)_{Ge}$ steps with a theoretical width of about 1.5 nm and edges parallel to the $[\bar{1}10]_{Ge}$ direction. The formation of a very regular step structure is confirmed by the splitting of the diffraction spots in the direction perpendicular to the step edges (*i.e.*, the $[11\bar{2}]_{Ge}$ direction).[33] However, the Ge(223) surface is characterized by a rather complex reconstruction which makes it quite difficult to disentangle the contribution from the surface superstructure and from diffraction from step edges. [34] The LEED patterns collected on the 10 nm thick Bi films are shown in Figure 1c,d. For what concerns the film grown on the Ge(111) surface, a diffraction pattern characteristic of the hexagonal Bi(111) phase is observed, in good agreement with the findings of Ref. [20] on the same system. The LEED image related to the Bi film grown on the Ge(223) surface, acquired in the same experimental condition of Figure 1b, is characterized by a noticeable splitting of some of the diffraction spots, but maintains the same hexagonal symmetry of the Bi film grown on flat Ge(111). It is possible to quantitatively estimate the splitting Q of the diffraction spots, which is about 0.3 Å^{-1}, corresponding to a step width in real space of about $2\pi/Q \cong 2$ nm,[35] in fair agreement with the result expected for a vicinal Bi surface showing BL-thick $(111)_{Bi}$ steps.

The result outlined above is a rather convincing evidence about the possibility of stabilizing a high index Bi(111) surface in a thin film grown on top of a semiconducting substrate. In the following, we proceed with a brief analysis of the spin-resolved electronic structure around the $\overline{\Gamma}$ point of the surface Brillouin zone (SBZ). The results are shown in Figure 2.
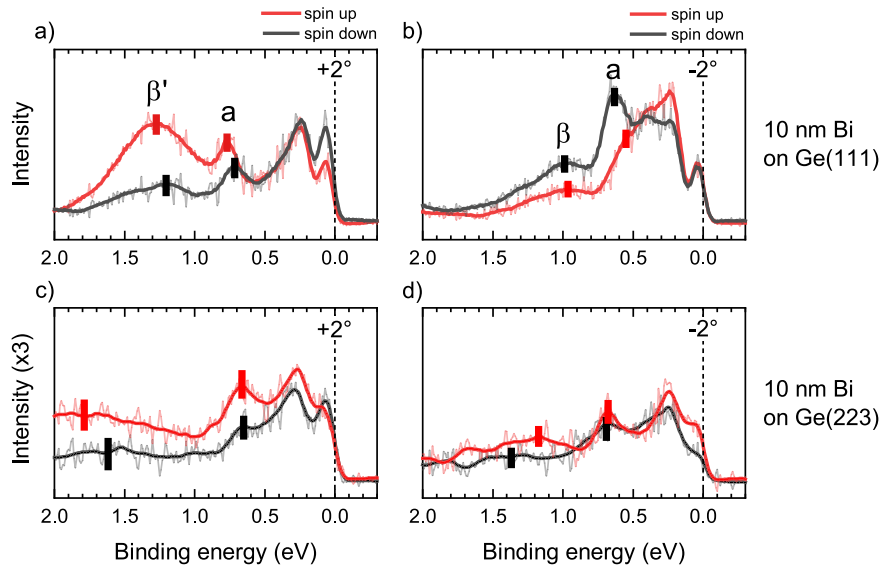

Figure 2. SR-PES spectra acquired on a 10 nm thick Bi film grown on a,b) Ge(111) and c,d) Ge(223) by tilting the sample by $\pm 2°$ towards the $[11\bar{2}]_{Ge}$ direction [*i.e.*, along the $\overline{\Gamma M}$ direction of the Ge(111) SBZ]. Here 0° means that the electrons are emitted along the $[111]_{Ge}$ direction, normal to the Ge(111) terraces. Spin "up" and "down" labels identify two opposite spin directions along the $[\bar{1}10]_{Ge}$ axis. Vertical bars mark the position of the spectral features discussed in the text. Thick lines are the result of a smoothing operation performed on the experimental data and are meant to guide the eye.

The spin-resolved photoemission spectra of Figure 2 are acquired by tilting the sample towards the $[11\bar{2}]_{Ge}$ direction, so that the component of the electron momentum within the surface plane ($\boldsymbol{k}_\parallel$) lies along the $\overline{\Gamma M}$ direction of the Bi(111) SBZ. The spin polarization of the photoemitted electrons is measured along the $[\bar{1}10]_{Ge}$ direction, *i.e.* perpendicular to $\boldsymbol{k}_\parallel$. The spectra related to the 10 nm thick Bi film on Ge(111) are reported in Figure 2a,b and are in fair agreement with the results of Ref. 36 related to a bulk Bi(111) sample, thus confirming our interpretation of the LEED picture of Figure 1c suggesting the stabilization of the Bi (111) surface. Owing to the three-fold symmetry of the bulk Bi(111) lattice, the energy dispersion of the bulk Bi states it is not symmetric with respect to the inversion of the electron momentum ($\boldsymbol{k}_\parallel$). This is clearly observed, for instance, for the bulk-derived states labeled a and β' in Figure 2a, and a and β in Figure 2b (following the nomenclature of Ref. 36). The observed spin polarization is a manifestation of the Rashba effect: within the adopted experimental configuration, a given electronic band is split into two branches populated by electrons with opposite

spins, thus producing a net spectral spin polarization which reverses its sign by crossing the $\bar{\Gamma}$ point ($\boldsymbol{k}_\parallel = 0$). Notwithstanding the different lineshape of the spectra reported in Figures 2a and b, the spin polarization of states a and β/β' is clearly reversed across the $\bar{\Gamma}$ point, as expected from the Rashba effect. As also reported in Ref. 36, the spin character of the states located close to the Fermi energy (E_F) is more difficult to assess, likely due to the finite angular resolution of the technique, together with their particularly asymmetric intensity distribution around the $\bar{\Gamma}$ point. Finally, we note that, while the Rashba effect is usually observed for surface states, in Bi also bulk states acquire a net spin polarization in proximity of the Bi(111) surface.[36]

Figure 2c,d presents our results on the 10 nm thick Bi film on the Ge(223) substrate. It is worth to recall that electrons photoemitted normal to the sample surface, *i.e.* along the $[223]_{Ge}$ direction, are characterized by not null component $\boldsymbol{k}_\parallel$ of the electron momentum with respect to the Bi(111) surface at the terrace scale. Therefore, in order to reach the $\bar{\Gamma}$ point (*i.e.* to photoemit electrons along the $[111]_{Ge}$ direction), the substrate was first tilted off normal by about $11.4°$ towards the $[11\bar{2}]_{Ge}$ direction. The two set of spectra of panels c and d were then acquired by adding an additional tilt by $\pm 2°$ in the same direction. As a result, the spectra acquired on both the 10 nm thick Bi films on Ge(111) and Ge(223) are representative of the same region in the momentum space. Also in the Ge(223) case, we can indeed recognize the spectroscopic signatures of states a and β/β'. However, by comparing the spectra of Figure 2c,d with their counterpart for the 10 nm thick Bi film on Ge(111) in Figure 2a,b, we observe much similar lineshapes with respect electron momentum inversion around the $\bar{\Gamma}$ point, *i.e.* in the direction perpendicular to the step edges, possibly due to a reduced asymmetry of the electronic bands in the Ge(223) case. The comparatively lower signal intensity and the different experimental geometry do not allow for a straightforward interpretation of the spin resolved spectra as in the case of the growth on the Ge(111) substrate. However, even if the net spectral spin polarization is not reversed across the $\bar{\Gamma}$ point, the binding energy position of the spin resolved electronic states associated with features a and β/β' follows the same characteristic ordering observed on the Bi film grown on flat Ge(111).

4. CONCLUSIONS

We have grown 10 nm thick Bi films on two different substrates, namely Ge(111) and Ge(223), at room temperature. The Ge(223) substrate is characterized by a regular distribution of steps along a well-defined crystallographic direction, interspersed with Ge(111) terraces. The surface crystallographic structure, checked by electron diffraction, is characterized in both cases by the characteristic hexagonal atomic arrangement of the Bi(111) surface. Similarly, the bandstructure close to the $\bar{\Gamma}$ point of the Surface Brillouin Zone is compatible with literature reports on bulk Bi(111), also for what concerns the fine structure resulting from spin-orbit effects. Interestingly, a noticeable splitting of the diffraction spots from the Bi surface is observed, strongly suggesting the successful stabilization of a stepped Bi(111) surface thanks to the regular perturbation to the film morphology induced by the use of a vicinal substrate. This is also likely reflected, on the same surface, in a reduced asymmetry of Bi electronic states with respect to the $\bar{\Gamma}$ point, in contrast to what is observed on flat Bi(111). The present result, *i.e.*, the realization of an ordered ensemble of step edges aligned along a well-defined crystallographic direction on the Bi(111) surface, is particularly appealing for both fundamental and applied studies, in view of the peculiar spin-related electronic properties (defect states, confinement effects, *etc.*) stemming from this morphology.

5. ACKNOWLEDGEMENTS

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