Orbital dependent Rashba splitting and electron-phonon coupling of 2D Bi phase on Cu(100) surface

Pierluigi Gargiani, Simone Lisi, Maria Grazia Betti, Amina Taleb Ibrahimi, François Bertran, Patrick Le Fèvre, and Letizia Chiodo

Citation: The Journal of Chemical Physics 139, 184707 (2013); doi: 10.1063/1.4828865
View online: http://dx.doi.org/10.1063/1.4828865
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/139/18?ver=pdfcov
Published by the AIP Publishing
Orbital dependent Rashba splitting and electron-phonon coupling of 2D Bi phase on Cu(100) surface

Pierluigi Gargiani,1 Simone Lisi,1 Maria Grazia Betti,1 Amina Taleb Ibrahimi,2 François Bertran,2 Patrick Le Fèvre,2 and Letizia Chiodo3

1Dipartimento di Fisica, Università di Roma “La Sapienza,” Piazzale A. Moro 5, I-00185 Roma, Italy
2Synchrotron SOLEIL, Saint-Aubin-BP 48, F-91192 Gif sur Yvette, France
3Center for Life Nano Science @Sapienza, Istituto Italiano di Tecnologia and European Theoretical Spectroscopy Facility (ETSF), Viale Regina Elena 291, I-00161, Roma, Italy

(Received 4 September 2013; accepted 22 October 2013; published online 11 November 2013)

A monolayer of bismuth deposited on the Cu(100) surface forms a highly ordered c(2×2) reconstructed phase. The low energy single particle excitations of the c(2×2) Bi/Cu(100) present Bi-induced states with a parabolic dispersion in the energy region close to the Fermi level, as observed by angle-resolved photoemission spectroscopy. The electronic state dispersion, the charge density localization, and the spin-orbit coupling have been investigated combining photoemission spectroscopy and density functional theory, unraveling a two-dimensional Bi phase with charge density well localized at the interface. The Bi-induced states present a Rashba splitting, when the charge density is strongly localized in the Bi plane. Furthermore, the temperature dependence of the spectral density close to the Fermi level has been evaluated. Dispersive electronic states offer a large number of decay channels for transitions coupled to phonons and the strength of the electron-phonon coupling for the Bi/Cu(100) system is shown to be stronger than for Bi surfaces and to depend on the electronic state symmetry and localization. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4828865]

I. INTRODUCTION

Adsorption of p-block elements on the low-index noble metal surfaces is able to induce peculiar phenomena or to enhance some specific couplings, such as large spin-orbit splitting of surface states,1,2 strong electron-phonon coupling (EPC),3,4 and surface Peierls instabilities.5 The formation of two-dimensional (2D) phases and the lacking of inversion symmetry for the electronic states can further influence these phenomena. In particular, the spin-orbit coupling (SOC) combined with the electric field induced by the surface discontinuity may give rise to the Rashba-Bychkov effect,6 as observed in several 2D semimetal systems.7–10 Furthermore, an enhanced electron-phonon coupling may appear for 2D electronic phases at interfaces, if dispersive electronic states offer a large number of decay channels for transitions coupled to surface phonons.3,4,11,12

All these effects can be rationalized as due to the formation of hybrid interface electronic states with strong surface localization, and thus an ideal 2D character, mainly due to the bonding between metallic states and adsorbate p orbitals. In particular, the formation of highly-dispersive electronic states with almost free-electron like parabolic dispersion is a common feature of 2D systems with high atomic number Z, as observed in Bi/Ag(100),13 Bi/Ag(111),1 Bi/Cu(111),14,15 Sb/Cu(111),15 Sb/Ag(111),16 Pb/Ag(111),2 and Bi/Si(111).17 For Bi surfaces, the spin-orbit splitting is fairly large owing to the heavy mass of the Bi atom. Bi surfaces also reveal a high density of states at the Fermi edge and a strong electron-phonon coupling, compared with values18–20 expected by considering the bulk behavior.

Bismuth 2D phases, supported on metal surfaces, present ordered superstructures or alloys of various symmetries. In the specific case of Bi deposited on the Cu(100) surface, the adatoms form highly ordered surface reconstructions at increasing Bi density. At half monolayer (ML) a c(2×2) phase with Bi atoms adsorbed on the hollow sites of Cu(100) surface has been observed, and at higher Bi density a domain-wall transition which results in the formation of lower symmetry c(9√2×√2)R45° and p(10×10) superstructures is induced.21,23,24

Aim of this paper is to investigate the electronic state dispersion of Bi-induced states in the energy region of the Fermi level and the electron-phonon response of a Bi single layer on the Cu(100) surface, unveiling its electronic structure at the light of the spin-splitting effect and EPC. We report a high resolution Angle Resolved Photoemission (ARPES) study of the Bi/Cu(100) c(2×2) phase, compared with density functional theory (DFT) calculations. We observe the presence of Bi-induced states with parabolic dispersion confined at the topmost surface layer and spin-split by Rashba effect, in agreement with the theoretical predictions. Furthermore, we determine the electron-phonon coupling parameters for Bi-induced states located at X and M on the Bi/Cu(100) c(2×2) phase, by means of temperature dependent photoemission measurements. The Bi c(2×2) phase presents a strong electron-phonon coupling mainly due to the delocalization of the Bi-induced states.

II. EXPERIMENTAL AND THEORETICAL DETAILS

Experiments have been carried out at the surface physics laboratory LOTUS, in Rome, and at the CASSIOPEE
beamline at SOLEIL synchrotron radiation storage ring. Photoelectron spectra have been excited with a He discharge lamp (HeI, and HeII photons, $h\nu = 21.218$ eV and 40.814 eV, respectively) in the LOTUS laboratory. The photoemitted electrons were analyzed in the plane of incidence, with a high resolution Scienta SES-200 hemispherical analyzer in the LOTUS laboratory and with a R4000 Scienta analyzer at CASSIOPEE. The analyzer slits at CASSIOPEE beamline were oriented parallel to the scattering plane allowing for full angular resolution measurements along the $\overline{X}$M symmetry line of Cu(100) Surface Brillouin Zone (SBZ). The overall energy resolution was better than 15 meV.

The high purity Cu(100) single crystal has been cleaned by sputtering-annealing cycles (Ar$^+$ ions, $E = 800$ eV, $T \sim 700$ K). High purity bismuth has been evaporated by means of a resistively heated quartz crucible and deposited on the substrate at RT, with an evaporation rate of about 0.5 Å per minute. The overlayer thickness has been determined with an oscillatory quartz microbalance. One monolayer is defined as the atomic density of $1.53 \times 10^{15}$ atoms/cm$^2$, corresponding to 5.4 Å of Bi.

*Ab initio* calculations in the framework of Density Functional Theory$^{25,26}$ have been performed to investigate the structural and electronic behavior of the Bi/Cu(100) interface, obtaining its equilibrium structure, the density of states, and the electronic band structure. For the sake of comparison with experimental data, we chose to analyze the $c(2\times2)$ geometry, as the simplest among the stable ones experimentally observed, and at the same time the one retaining most information on SOC effects and Rashba splitting. We used the plane-wave code Quantum-ESPRESSO,$^{27}$ the Perdew-Burke-Ernzerhof (PBE) approximation$^{28}$ for the exchange-correlation functional, and fully relativistic Cu and Bi ultra-soft pseudopotentials$^{29}$ (US-PPs) (cutoff of 45 Ry). Following the scheme reported in Ref. 30, the SOC by fully relativistic US-PPs has been included via density functional theory based on two-component spinor wave functions, on the same foot as done for unconstrained noncollinear magnetism. An 11 layer thick slab of Cu has been considered with a vacuum region of $\geq 10.0$ Å. All layers were allowed to relax perpendicularly to the surface. A $(10 \times 10 \times 1)$ K-point mesh has been employed.

**III. RESULTS AND DISCUSSION**

A 0.5 ML of Bismuth deposited on Cu(100) surface induces a highly ordered 2D phase with $c(2\times2)$ reconstruction, as deduced by the sharp spots in the Low Energy Electron Diffraction pattern, shown in Fig. 1(a). It is known from STM$^{33}$ and Grazing Incidence X-Ray Diffraction (GIXD) results$^{31}$ that the Bi atoms in the $c(2\times2)$ phase sit in the hollow sites of the Cu(100) surface lattice (Fig. 1(b)).

DFT calculations are used to provide the structural configuration of the Bi overlayer in the 2D $c(2\times2)$ phase, with the Bi atoms allocated in the hollow sites of the underlying Cu(100) surface, as known from previous experimental results.$^{23,31}$ The quasi 2D electronic charge density allocated in the topmost layers is modulated by charge depletion and accumulation, as can be clearly deduced by the charge density difference ($\Delta \rho = \rho_{Bi/Cu} - \rho_{Cu} - \rho_{Bi}$) plot reported in Fig. 1. The charge accumulation is mostly located at the Cu/Bi interface plane and outside the surface, and the charge oscillations become negligible at the third Cu layer below the surface. The presence of a confined charge distribution, associated with Bi electronic states, is a clear signature of an ideal 2D Bi phase, with free-electron like states almost floating on the Cu(100) surface. Similar charge rearrangement, for shape and intensity, has been obtained via DFT calculations$^{32}$ for Bi/Cu(111) and Bi/Ag(111) interfaces, both of them characterized by a strong spin-orbit coupling induced by Bi atoms.

Photoemission spectra of clean Cu(100) surface and of Bi/Cu(100) $c(2\times2)$ phase at $\overline{M}$ and $\overline{X}$ high symmetry points of the SBZ are reported in Fig. 2. The spectral density of Cu(100) at $\overline{M}$ point (Fig. 2(a)) presents a huge surface feature at 1.79 eV binding energy (BE), when excited with the electric field parallel to the surface plane, consistently with previous photoemission data.$^{33}$ This state is attributed to the Tamm surface state $S_T$, with $d_{x^2−y^2}$ symmetry.$^{33}$ A second surface feature, located at 2.06 eV BE and close to the bulk band projection B$_{Cu}$,$^{33}$ is attributed to a Shockley state $S_S$. Upon Bi deposition, a quenching of the Tamm state occurs, and a Bi-induced state, $E_1$, at 2.09 eV, is observed, in agreement with a recent photoemission study.$^{34}$ The intensity of $E_1$ peak is maximum for vertical polarization (the electric field lying in the surface plane). In Fig. 2(b) the spectral density of Cu(100) is compared with the Bi/Cu(100) $c(2\times2)$ phase at $\overline{X}$ point. The Cu(100) is characterized by two intense bulk projected states.$^{33,34}$ Upon Bi deposition, four Bi-induced peaks arise, namely $E_2$, $E_3$, $E_4$, and $E_5$, at 1.74 eV, 1.69 eV, 1.19 eV, and 0.97 eV of binding energy, respectively. These Bi-induced features are intense if excited by light polarized in the surface plane.
The surface band dispersion along the XM direction is shown in Fig. 3. We plotted the second derivative of the PES intensity to enhance weak features. The most intense states E2, E4, and E5 present a defined free-electron like dispersion along the XM direction. In particular E2 and E5 have an upward dispersion, with a positive electron effective mass of $1.30 \pm 0.02$ and $0.53 \pm 0.03 \text{m}^* m_e$, respectively, as estimated by a parabolic fitting. The E4 state presents a downward dispersion, with a negative effective mass of $0.21 \pm 0.01 \text{m}^* m_e$. Notably, along the XM line, we can distinguish two weak features, named E6+ and E6-, symmetric with respect to XM, with a parabolic-like dispersion and the minimum centered at $\pm 0.32 \text{Å}^{-1}$ along the XM line. This band shape is a distinctive signature of Rashba spin-splitted states.

A deeper understanding of Bi spin-orbit effects can be achieved by ab initio DFT calculations, compared with angular resolved photoemission spectra.

The band structure calculated for Bi/Cu(100) c(2×2) along the direction XM observed in the experiment (corresponding to $\Gamma X$ of the $(2 \times 2)$ surface cell used in the calculation), without the inclusion of spin-orbit coupling, is reported in Fig. 4(a) and it is in fair agreement with previous non-relativistic DFT calculations. Only states with a major contribution from Bi atoms are shown, even if most of them are constituted by admixtures with Cu derived states. We did not apply a correction to the energy levels from DFT to align them to experimental data, as the DFT underestimation of the binding energies with respect to the experimental values will be not just a rigid shift, but will depend on the symmetry and wave function components of the considered electronic state.

The most intense state, N2, is mainly related to Bi $p_{x,y}$ states hybridized with $d_z^2$ and $d_{x^2-y^2}$ Cu components, mostly distributed in the surface plane. The other three parabolic states, N3, N5, and N7, are mainly of $p_z$ symmetry, involving $d$ levels from Cu atoms in the second layer below the surface. The negative effective mass states N3 and N4 are mainly characterized by $p_{x,y}$ and $p_z$ symmetry wave functions, respectively and both states show a contribution coming from Cu $d_{x^2}$ and $d_{x^2-y^2}$ symmetry Cu states.

When the spin-orbit coupling is included in the DFT calculations, the band structure becomes more complex due to the splitting of the different J components of the bands (reported as blue and red in Fig. 4(b)). Comparing the theoretical band structure with the experimental spectral density shown in Fig. 3 we can easily identify the correspondence between the Bi-induced states. A striking evidence of the good agreement among theoretical band dispersion and experimental spectral density is the prediction of the Rashba-splitted bands. In fact the S6 state, with its parabolic minimum out of XM, due to a Rashba splitting, is in close correspondence with the experimental peak Eo.

The most notable effects of the SOC and Rashba splitting are observed on the $p_{x,y}$ states (N2, N3) where the SOC induces the angular momentum degeneracy removal and the surface localization of the wavefunction determines a Rashba splitting of the electron energy bands. The band S3 is the SOC equivalent of the N1 state. For this state, both energy and momentum shifts are observed, as the angular momentum degeneracy is removed by the spin-orbit interaction, and the k shift is induced by the Rashba effect. Two bands with the same negative curvature near the $\Gamma$ point can be identified. The higher lying has its maximum at energy $-1.26 \text{eV}$ and has an $m_j = 3/2$ character, the second has its maximum at $-1.57 \text{eV}$ and $m_j = 1/2$.

These theoretical assignments can be compared with previous experimental results on analogous systems. The energy separation between the two bands $\Delta E = 0.31 \text{eV}$ is lower than the one calculated for the Bi/Ag(111) alloy ($\sim 0.7 \text{eV}$) and higher than for Bi crystal surfaces. A closer look at the two branches of the $S_3$ band brings to light a band inversion.
FIG. 4. DFT calculated band structure projected along the $\overline{X}\overline{M}$ direction for Bi/Cu(100) $c(2\times2)$ (a) not including the spin-orbit coupling and (b) including the spin-orbit coupling. Red denotes Bi states with $m_j$ equal to 1/2; blue stands for $m_j$ equal to 3/2.

point, out of the $X$ point. The band maximum is located at $\pm 0.06 \, \text{Å}^{-1}$ for both the bands indicating a weak Rashba splitting.

The states $S_2$ and $S_6$ closely correspond to $E_2$ and $E_6$ of Fig. 3 and they cannot be easily related to states in the band structure without the spin-orbit coupling. It is worth to notice that $S_2$ and $S_6$ originate from the splitting of $N_2$ band and they are strongly hybridized with other Bi derived states, as observed in the Bi/Ag(111) and Pb/Ag(111) alloy systems. In particular, the wavefunction of $S_6$ is mainly of $p_{x,y}$ symmetry with $m_j = 1/2$ and defined spin orientation. In fact, if we choose a spin quantization axis parallel to the surface plane and perpendicular to the $k_||$ direction, the spin changes sign according to $k_||$, indicating a Rashba origin of the $S_6$ bands. The other component $m_j = 3/2$ of the $N_2$ band is therefore associated to the $S_2$ state that shows an almost complete $m_j = 3/2$ character and an energy separation from $S_6$ that can be roughly estimated to be of $0.30 - 0.40 \, \text{eV}$.

The parameter $\alpha_R$ that describes the momentum separation of the two spin directions of $S_6$, derived in the approximation of a free-electron like dispersing state, is given simply by $\alpha_R = \hbar^2 k_0/m^*$, where $k_0$ is the momentum separation from the high symmetry point of the splitted bands along the $XM$ direction and $m^*$ is the effective mass of the band. Within this approximation, from the experimental data, $m^* = 0.82 \pm 0.08 \, m_e$ and $k_0 = 0.32 \, \text{Å}^{-1}$ and the Rashba parameter is $\alpha_R = 3.01 \pm 0.06 \, \text{eV} \, \text{Å}$ for $E_6$. The DFT calculations predict for $S_6$ $K_0 = 0.36 \, \text{Å}^{-1}$ and a Rashba parameter $\alpha_R = 3.2 \, \text{eV} \, \text{Å}$, in very good agreement with the experiment and the result can be rationalized in terms of the almost pure 2D character of the Bi-induced features at $\overline{X}$ point. This value is larger than $\alpha_R$ for Bi(111) surface $^{19}$ (0.56 eV Å), and of the same order of the values obtained for other Bi/metal interfaces and alloys, as Bi/Cu(111)$^{15}$ (1.00 eV Å) and Bi/Ag(111)$^1$ (3.05 eV Å).

The $p_z$-Bi derived states ($S_4, S_5, S_7, S_8$), easily associated to their non-SOC counterparts ($N_4, N_5, N_7, N_8$), correspond to the $E_4$ and $E_5$ experimental dispersive bands of Fig. 3. These states should not in principle be affected by the Rashba splitting, because of the symmetry with respect to the plane of charge rearrangement. Around $\overline{X}$, the $m_j$ component of $S_5, S_7$, and $S_9$ is 1/2, but they hybridize with $m_j = 3/2$ states moving from $\overline{X}$ towards the zone boundary.

To resume this first part of results, the theoretical band mapping and the photoemission spectral density reveal a 2D Bi phase, whose electronic states with strong surface localization are mainly due to the bonding between metallic states and $p$ orbitals from the Bi adatoms. The formation of highly-dispersive electronic states with almost free-electron like parabolic dispersion, observed in other Bi 2D phase on metals,$^{1,13-15}$ is affected by a Rashba splitting when their charge density is strongly localized in the Bi plane. The comparison between SOC and non-SOC DFT calculated band dispersion can be rationalized in terms of symmetry of the electronic states and it allows a detailed identification of features observed in the photoemission spectra.

A further insight of the unique properties of this class of 2D Bi systems can be obtained by investigating the electron-phonon interaction. The temperature dependence of the linewidth of photoemission features$^4$ is a reliable tool to investigate the electron-phonon coupling at interfaces.

The Bi-induced electronic states at $\overline{M}$ point and $X$ point have been studied as a function of temperature in the 8–300 K and 30–320 K ranges, respectively. The analysis has been
performed at the high symmetry points $\mathbf{M}$ and $\mathbf{X}$, considering interface electronic states with a spin-dependent dispersion ($E_4$ and $E_5$) at $\mathbf{X}$ and $E_1$ at $\mathbf{M}$. The analysis is based on the fact that the temperature dependent Lorentzian linewidth $\Gamma$ of a surface state, extracted from the energy distribution curve, is a direct probe of the inverse of the photohole lifetime. The electron-electron (EE) and the electron-impurity (EI) interactions are almost independent of temperature and only the electron-phonon (EP) scattering probability can be related to temperature, as the occupation number of phonon modes depends on temperature. In the Debye approximation, the EP scattering probability can be related to temperature proportional to the density of phonon modes:

$$\Gamma = 2\pi \lambda K_B T,$$

where $\lambda$ is the EPC mass enhancement parameter $m^* = m (1 + \lambda)$.

The photoemission peaks have been fitted with a Voigt lineshape (Gaussian-Lorentzian convolution), taking into account the finite experimental resolution (13 meV). The temperature evolution of the Bi-induced states $E_1$, $E_4$, and $E_5$ at $\mathbf{M}$ and $\mathbf{X}$ are reported in Figs. 5(a) and 5(b). The Lorentzian linewidth, as a function of sample temperature, is reported in panels (c) and (d) of Fig. 5. The linear slope of the Lorentzian linewidth of peak $E_1$ versus temperature leads to a $\lambda_1$ value of $0.32 \pm 0.01$. The width reaches a constant value (30 meV) for temperatures $\leq 20$ K, and it can be attributed to the almost temperature independent electron-electron and electron-impurity scattering contributions to the photohole lifetime. For comparison we report the temperature dependence of the Cu Tamm state, in agreement with previous results.

The temperature evolution of the Lorentzian linewidth of spectral features $E_4$ and $E_5$ at $\mathbf{X}$ point (Fig. 5(b)) allows to estimate $\lambda$ as $0.9 \pm 0.1$ for $E_4$ state and $1.1 \pm 0.1$ for $E_5$ state. These electron-phonon mass enhancement values measured at $\mathbf{X}$ indicate a larger phonon mediated decay channel with respect to the state $E_1$ located at $\mathbf{M}$. At the $\mathbf{X}$ point of the SBZ the presence of dispersive energy bands can enhance both small and large momentum scattering events, and the co-presence of intraband and interband transition.

High $\lambda$ values have been previously reported for the following Bi surfaces: $\lambda = 0.72$ for the Bi(100) surface, and $\lambda = 0.6^{37}$ or $\lambda = 0.4^{36}$ for the Bi(111); while $\lambda$ is expected to be lower in the Bi bulk ($\lambda = 0.13^4$). Moreover a high electron-phonon coupling has been reported for the surface alloy Bi/Ag(111) system, for which recent temperature dependent photoemission data from Guan et al.\textsuperscript{39} provide a value of $\lambda \simeq 0.55$. Bi surfaces are characterized by an enhanced density of electronic states that can induce a more effective coupling with the lattice vibration offering more channels for the electron excitation and de-excitation.\textsuperscript{3,4} The surface vibrational modes can strongly enhance the coupling constant $\alpha_R$ of the Eliashberg function\textsuperscript{3,40} for electronic states with charge density localized in the first atomic layers, as observed for Bi surfaces.\textsuperscript{18,19,37,41,42}

The driving factor for the EP coupling of these Bi 2D systems is the well defined charge localisation confined in the first layers, as clearly demonstrated in the charge density difference, $\Delta \rho$, induced by the adsorption of a single layer of Bi on Cu(100) (Fig. 1).

For a deeper understanding of the driving forces leading to the electron-phonon coupling strength enhancement, first-principle calculations of the phonon spectrum and the Eliashberg coupling function would be required. However, the coexistence of strong EPC and spin-orbit interactions can influence the electron localization giving rise to other effects, like the formation of small polarons if the electron-phonon coupling $\lambda$ is higher than 0.5. In a future work, it will be interesting to explore how the electron-phonon interaction would influence polaron formation.

IV. CONCLUSIONS

The electronic state dispersion of c(2×2) Bi/Cu(100) re-constructed phase has been investigated by means of angular resolved photoemission and density functional calculations. The almost free-electron like dispersion of Bi-related states is a consequence of the charge delocalization among the atoms of the Bi 2D overlayer, almost floating on the underlying Cu layer. The presence of surface confined, free-electron like dispersion bands justifies the Rashba type splitting of the electronic states, triggered by the large atomic SOC of Bi. The Rashba $\alpha_R$ parameter is large compared to Bi metal surfaces and Bi/metal interfaces, and we relate it to the almost pure 2D character of the Bi-induced features at $\mathbf{X}$ point.

The electron-phonon coupling has been studied by means of temperature dependent photoemission spectroscopy, and electronic states close to the Fermi level are characterized by a stronger electron-phonon interaction, rationalized by the larger energy and momentum delocalization of the Bi-induced
states in the c(2\times2), compared to the Bi surfaces or other Bi/metal interfaces.

The strength of the spin-splitting, the electron-phonon interaction and the localization of the semimetal induced states can be tuned in these 2D phases via adsorption on different substrates with different interaction strengths.

ACKNOWLEDGMENTS

L.C. wishes to thank CINECA supercomputer center for cpu-time (ISCRA-CINECA project q2D-FUSS).