One-Dimensional "Dislocation-Related" Electronic States at the GaAs(110)-Bi(1×1) Interface

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(Received 12 August 1991)

We present a high-resolution electron-energy-loss-spectroscopy investigation of the GaAs(110)-Bi(1×1) interface system. Exploiting *p*- and *n*-type doped substrates, the Fermi-level pinning position could be related to the electronic surface states produced by the misfit dislocations of the semiconducting Bi epitaxial monolayer. For the first time electronic transitions involving *one-dimensional dislocation-related states* are brought into evidence, in particular after an adequate thermal treatment of the interfaces that produces a long-range ordering of the dislocations.

PACS numbers: 73.20.Dx

The chemisorption of group-V semimetals on III-V compound semiconductors has received much attention in the last few years, owing to the unreactive, nondisruptive, and ordered nature of the interfaces formed. In fact, such systems constitute a model situation in which a strict relationship between structure and electronic properties can be sketched. Antimony forms an ordered structure when deposited on the (110) face of GaAs, at the completion of one monolayer (ML). Sb atoms build up regular chains on top of the surface Ga and As atoms along the $[1\bar{1}0]$ crystallographic direction. The observation of this has been accomplished mainly through electron spectroscopy measurements [1–8] and band-structure calculations [9–11]. The analogous interface established by bismuth on GaAs(110) also forms a regular and ordered monolayer [12–17]; however, the linear chains are periodically interrupted by ordered arrays of dislocations. A clear image of such dislocations has been achieved through scanning tunneling microscopy (STM) [18,19]. These dislocation arrays are due to the lattice mismatch of the Bi overlayer. For diminishing the surface strain, the semimetal overlayer forms periodical rows of missing Bi atoms in the (100) direction.

Annealing, at adequate temperature, of a 4-ML-thick Sb layer produces a very ordered monolayer, more regular at long-range scale than the as-deposited monolayer [2,4,8]. Bismuth does not behave like antimony when a 4-ML-thick layer is annealed at appropriate temperature. Similar to Sb, all Bi in excess of 1 ML desorbs [15], but the monolayer is not more ordered than the "as-deposited" one. Photoemission measurements on annealed layers of Bi deposited on GaAs(100) were interpreted assuming Bi clustering on top of the first epitaxial ML [20]. For the (110) surface too, annealing seems not to improve substantially the epitaxial structure of the overlayer, though low-energy electron diffraction (LEED) studies detected clear sixth-order satellite spots [13,16]. These extra features are superimposed on the still distinct (1×1) pattern but are more elongated than the integral-order spots. They correspond to an ~24 Å periodicity and were attributed to the periodic rows of missing Bi atoms observed by STM [18,19]. Hence, annealing does not improve the (1×1) epitaxial order, even if it seems to facilitate a long-range ordering of the periodic dislocations.

The electronic states associated with the regular two-dimensional (2D) Bi monolayer on the (110) surface on GaAs were measured by direct [15,17] and inverse [14] photoemission, and by STM spectroscopy [18,19]. Angular-resolved photoemission allowed one to follow the dispersion of the highest Bi-derived 2D occupied bands along the main crystallographic directions [17]. Apart from finer considerations on the symmetry of such states [17], a close analogy can be sketched with the corresponding states of the ordered Sb adlayer [1,4,9,10]. Using the labeling of band-structure calculations [9,10] and STM spectroscopy [18,19], the uppermost occupied Bi S_6 state lies close to the GaAs valence-band maximum (VBM) while the lowest unoccupied S_7 level is close to the GaAs conduction-band minimum (CBM), and both extend to some extent into the semiconductor band gap. Clear evidence of an electronic transition between S_6 and S_7 was found in a high-resolution electron-energy-loss-spectroscopy (HREELS) study of the same system [21] and an interface energy gap of 0.65 eV was estimated, confirming the semiconducting character of the GaAs(110)-Bi(1×1) monolayer system.

HREELS is an efficient probe for investigating the electronic properties of clean semiconductors and their interfaces. It was successfully used to determine the azimuthal anisotropy of the electronic structure of the clean-cleaved GaAs(110) relaxed surface [22], as well as the electronic transition associated with the Sb-derived S_6 and S_7 states in the InP(110)-Sb(1×1) semiconducting monolayer [23]. We decided, therefore, to apply this spectroscopy to the Bi-GaAs interface, focusing our attention in particular on the electronic properties at low energy. Along with the main absorption edge at 0.65 eV, distinct new structures are singled out at lower energy, associated with electronic levels located at the dislocations of the ordered Bi adlayer. HREELS measurements performed on both *n*- and *p*-type doped GaAs are discussed along with STM spectroscopic results [18,19] and give some new information on the mechanisms driving the Fermi-level pinning on this interface. The new low-energy absorption structures are related to states induced at the rows of missing Bi atoms. Annealing influences the structural order and these electronic transitions, revealing

the presence of one-dimensional (1D) states produced at the dislocations.

Experiments were carried out at the surface physics laboratory Spettroscopia Elettronica Superfici Adsorbati of the Dipartimento di Fisica, Università di Modena. HREELS measurements were done with a Leybold-Heraeus ELS-22 spectrometer in an ultrahigh-vacuum (UHV) system, also equipped with LEED, photoemission, and other facilities for sample preparation. The base pressure was 7×10^{-11} mbar (7×10^{-9} Pa) and it rose to 3×10^{-10} mbar during Bi evaporation. GaAs(110) surfaces were prepared by cleavage in UHV with the single-wedge technique. The GaAs bars were of p-type (Zn, 2×10^{19} cm^{-3}) and n-type (Te, 2.7×10^{18} cm^{-3}) doping. Surface crystalline order was observed by LEED, prior to and after Bi deposition. Cleanness was measured by HREELS and photoemission. Bi was evaporated from a resistively heated quartz crucible, at a rate of the order of $\sim$1 Å/min. Thickness was monitored with a cooled quartz microbalance after calibration by photoemission. One Bi monolayer was defined as one Bi atom for each surface substrate atom (atomic surface density 8.85×10^{14} cm^{-2}). HREELS data were taken in the specular direction, with an angle of incidence of 63° and primary beam energies of 15 and 20 eV. The energy resolution was about 20 meV, ensuring an opportune signal intensity.

The HREELS measurements for 1 ML Bi on p- and n-type GaAs(110) as-deposited are shown in Fig. 1, in the 0–1-eV energy-loss region. A huge loss structure emerges at about 0.85 eV for both the substrates, while a weak feature is present at about 0.55 eV only for the interface with p-type GaAs. We deposited an additional 3 ML of Bi on both the substrates and annealed at $\sim$285 °C for $\sim$15 min. For the sake of simplicity we shall call this kind of preparation "annealed Bi." After this procedure all bismuth in excess of 1 ML desorbed from the surface and a distinct (1×1) LEED pattern was obtained, along with a lighter but clear (6×1) superstructure along the [1$\bar{1}$0] azimuthal direction, in agreement with previous results [13,16]. The HREELS data relative to the annealed Bi on p- and n-type doped GaAs are shown in Fig. 2, in the 0–1-eV energy-loss region. The huge absorption structure at $\sim$0.85 eV is still present, as in the as-deposited case, while the 0.55-eV loss structure, previously detected only on the p-type substrate, gains intensity and a new broad feature emerges at about 0.35 eV for the n-type substrate. The 0.85-eV structure, common to both substrates and 1-ML preparations, is clearly related to an electronic transition between Bi levels in the epitaxial structure built up on GaAs(110). It is evidence of the semiconducting nature of the Bi single monolayer, as discussed in a previous work [21], and it depends nei-

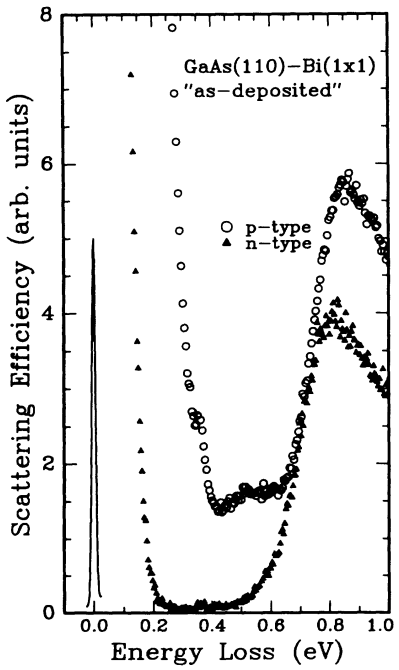

FIG. 1. HREELS (scattering efficiency) data relative to the 1-ML-Bi interface with GaAs(110) "as-deposited" on p- (above) and n- (below) doped substrates. Data are enlarged by a factor of 2000 with respect to the elastic peak intensity and normalized to the main structure at about 0.85 eV. Spectra are displaced along the vertical axis for convenience.

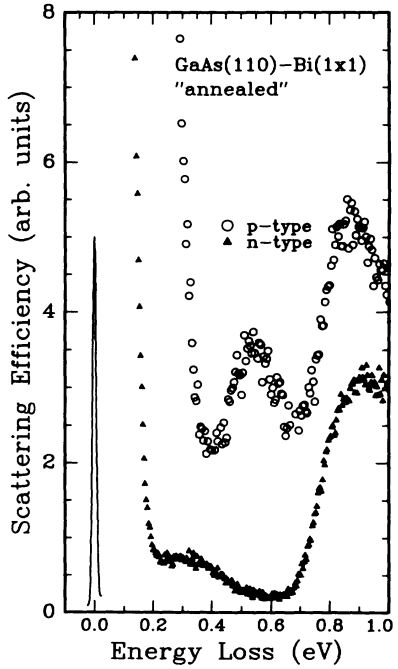

FIG. 2. HREELS (scattering efficiency) data relative to the 1-ML-Bi interface with GaAs(110), obtained after appropriate annealing of a 4-ML-thick Bi layer ("annealed Bi"), on p- (above) and n- (below) doped substrates. Data are enlarged by a factor of 2000 with respect to the elastic peak intensity and normalized to the main structure at about 0.85 eV. Spectra are displaced along the vertical axis for convenience.

ther on the substrate doping nor on the procedure of monolayer preparation. Hence, it is very likely related to the main band-gap absorption of the semiconducting GaAs(110)-Bi(1×1) interface [24] taking place between the Bi S_6 level, lying near the GaAs VBM [15,17–19], and the empty Bi S_7 electronic state, lying close to the GaAs CBM [14,18,19].

What about the lower lying electronic transitions? STM spectroscopy measurements [18,19] showed a finite conductivity signal in the band-gap region, extending between the Bi S_6 and S_7 levels. These very interesting structures at midgap were found only near the Bi dislocation arrays and were attributed to the Ga dangling and Bi broken bonds at the missing Bi rows. There is an energy difference for the Fermi-level pinning on p- and n-type GaAs [see Fig. 7(c) of Ref. [18]]. In fact, the Fermi-level position for the n-doped substrate (E_n^F) could be determined within the midgap states, whereas the Fermi level for the p-type GaAs (E_p^F) was found 0.2 eV underneath E_n^F, pinned by the top of the interface VBM, corresponding to the top of S_6. Owing to the Fermi-level pinning difference of ~200 meV occurring between the p- and n-type substrates, such "dislocation-related" states were found to be empty for the p-type and only partially occupied for the n-type substrate, having mainly an acceptorlike character. Therefore, the peak at 0.55 eV for the p-type substrate (Fig. 1) can be attributed to the electronic transition from the filled Bi S_6 state (VBM of the system) to the midgap acceptorlike states. The higher intensity of this transition for the annealed Bi (Fig. 2) can be explained by supposing that the joint density of states (JDOS) available for the transition increases with annealing. Assuming that annealing provokes a long-range ordering of the dislocations in the Bi overlayer, as deduced by LEED, we can estimate the density of the dislocation-related states. A dislocation row every 24 Å leads to a density of $\sim 7\times 10^{13}$ cm^{-2} missing Bi atoms on the surface. Provided that each Bi vacancy produces only one acceptorlike state, the density of acceptor states rises to ~8% of the GaAs surface states, which could explain the enhancement of the HREELS peak for the annealed Bi with respect to the as-deposited Bi. As a matter of fact, the ordering of the dislocations seems to produce actual *extended one-dimensional electronic bands,* as deduced from the higher JDOS originated by the thermal treatment.

For the n-type GaAs the situation is completely different. Because of the higher-energy position of the Fermi level E_n^F, lying within the dislocation-related states distribution [18,19], transitions can take place between the occupied part of such states (with a donorlike character) and the continuum of empty states of the Bi-GaAs semiconducting system extending into the gap. However, the strength of these interband transitions seems to be extremely low, as no clear structure emerges below the main absorption edge (Fig. 1), probably due to the low density of initial states. Only for the annealed Bi monolayer, given the increased number of dislocation-related states, do we measure a structure whose centroid is at ~0.35 eV (Fig. 2). The presence of a peaked structure at this energy makes it very improbable that there are intraband transitions between the partially filled and empty parts of the above described states. Again, we can conclude that the ordering of the dislocations, driven by annealing, produces actual *extended 1D electronic bands,* and interband transitions having such levels as initial states become detectable. Moreover, these measurements confirm that this is a semiconducting interface, and the role of the dislocation-related states is fundamental in establishing the final pinning of the Fermi level at the coverage of one monolayer.

The intensity of the dislocation-related transitions may appear very high in the annealed Bi, with respect to the main absorption structure, even considering that the dislocation-related states can be at most 8% of the surface states involved in the main electronic transition. An explanation can be found in the kinematics of a HREELS experiment. In fact, the scattering efficiency S_E of HREELS data can be factorized, in a first approximation, as $S_E = KL/RI_0$, where K is the kinematic prefactor (KF), a function of the primary beam energy, the angle of incidence, and the loss energy; R is the reflectivity of the system at that energy, assumed to be constant in this energy range; and I_0 is the intensity of incoming electrons. L is the so-called loss function (LF) and is correlated to the absorption of the system [25]. Having normalized the spectra to the elastic peak intensity RI_0, we divided the data by the appropriate KF—given the actual experimental conditions—and obtained the LF. The result of this procedure is shown in Fig. 3, where we plot the LF for the annealed Bi overlayers on both p- and n-type systems. Even if no absolute comparison can be made, the intensity of the LF structures in the 0–1-eV energy range is much closer to the expected intensity of the respective transitions than the corresponding intensity of the S_E structures of Fig. 2. In particular, the intensity ratio of the 0.35- to the 0.85-eV structure is lower for the LF than for the S_E, for the p-type system. The analogous ratio is even more reduced for the n-type system. This is consistent with the expected DOS associated with the 1D bands involved in the low-energy transitions. Moreover, the extrapolation to low energy of the LF structures can give an approximate value of the absorption edge, resulting in 0.65 eV for the main absorption structure on both systems [24], and 0.41 and 0.23 eV for the dislocation-related absorption structures in the p- and n-type systems, respectively.

In conclusion, HREELS measurements on GaAs(110)-Bi(1×1) interface systems for p- and n-type doped substrates brought into evidence electronic transitions below the main absorption edge of the semiconducting epitaxial Bi monolayers. These low-energy transitions involve *dislocation-related electronic levels* located at the dangling and broken bonds in the rows of missing Bi atoms.

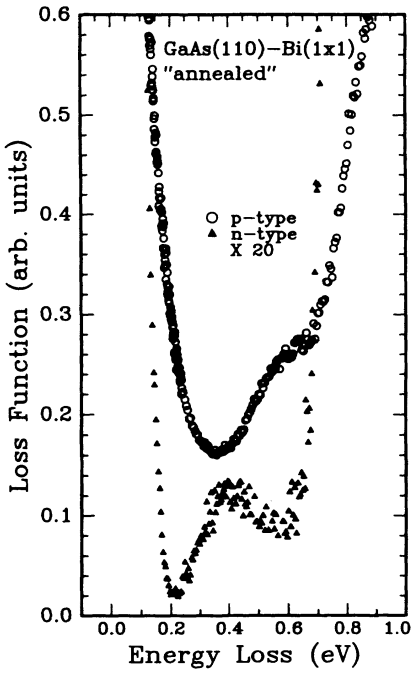

FIG. 3. Loss-function data relative to the 1-ML-Bi interface with GaAs(110), obtained after appropriate annealing of a 4-ML-thick Bi layer ("annealed Bi") on *p*- (above) and *n*- (below) doped substrates. Data are normalized to the main structure at about 0.85 eV, but the spectrum relative to the *n*-type substrate (below) is magnified by a factor of 20. Spectra are displaced along the vertical axis for convenience.

An appropriate annealing procedure determines a *long-range ordering of the dislocations* and a consequent increase of their density per unit surface, producing *1D electronic bands* along the rows of missing Bi atoms. Azimuthal-resolved measurements on the Bi monolayer prepared via annealing would be extremely useful for a further characterization of the symmetry properties of such 1D bands. The pinning of the Fermi level is driven by these dislocation-related states on both *p*- and *n*-type systems.

Suggestions and discussions with Maria Grazia Betti are gratefully acknowledged, and thanks are due to E. Angeli for experimental assistance. Funding came partially from the Consiglio Nazionale delle Ricerche (CNR) and the Ministero per l'Università e per la Ricerca Scientifica e Tecnologica (MURST). We also thank the Commission of the European Communities for a grant given to R.C.

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