Au/n-ZnSe contacts studied with use of ballistic-electron-emission microscopy

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Ballistic-electron-emission microscopy (BEEM) has been used to study the Schottky-barrier formation at the Au/n-ZnSe interface. Spectroscopy measurements indicate that the Schottky-barrier heights present unusually large variations and range from 1.53 to 2.15 eV. The lowest values are in good agreement with the barrier heights obtained from macroscopic current-voltage (I-V) measurements. The possible reasons for the existence of large Schottky-barrier variations are presented and discussed in this paper. These include the effect of variations of the work function and the behavior of the contact as a metal-insulator-semiconductor structure due to microclusters of different phases at the interface. Contrasts in the BEEM image are also found to follow the gold grain boundaries and are assumed to depend both on the grain orientation and interface quality.

INTRODUCTION

In scanning tunneling microscopy (STM) and related techniques, local fields in the close vicinity of the surface are probed by a very sharp probe. In STM, the tip scans a conductive surface and detects the height variations owing to the variations of the tunneling current that occur when the two electron clouds of each electrode overlap.[1] The resolution yielded is in the subnanometer range when the tip is terminated by only one atom. However, these techniques concern only the surface itself or the first layers below this surface.

In 1988, Kaiser and Bell used ballistic-electron-emission microscopy (BEEM) to study the buried interface between a metal and semiconductor.[2,3] The tip of the STM then acts as a local electron emitter to yield depth information of material. The BEEM working principle implies that two conditions are fulfilled. The first one concerns the metal layer thickness, which should not exceed the electron mean free path in the overlayer, which is less than 100 nm for electron energies of the order of few eV.

The second condition concerns the electron energy. The injected carriers should have a sufficient incident energy (given by the bias voltage V_s) to overcome the Schottky-barrier height (ϕ_b) at the interface. This gives the most important energy condition for detecting a collected current in the semiconductor: $|eV_s| \geq \phi_b$. Because carriers with a large $k_\parallel$ momentum (i.e., momentum parallel to the interface) are reflected in the metal layer, ballistic electrons probe a very small contact area at the interface with a lateral resolution of less than 2 nm.

This sensitivity explains why BEEM has been used to study many metal-semiconductor contacts. Most of these deal with elemental or III-V semiconductors such as Si,[2–7] GaAs,[8,9] or GaP.[10,11] However, little attention has been given to II-VI compounds, and the sole application concerns the work of Williams[12] and Fowell *et al.*[13] on Au/CdTe interfaces. In particular, they demonstrated that Schottky-barrier heights presented local variations, typically from 0.687 to 1.073 eV on a surface of 20×40 nm^2. The BEEM images showed very localized contrast, and the low barrier regions were associated with tellurium precipitates at the interface.

In this paper, we present investigations on Au/n-ZnSe contacts by BEEM. The Schottky-barrier height is found to vary significantly at the interface with lowest values in good agreement with macroscopic (I-V) measurements (≈1.6 eV). Unexpectedly, thresholds beyond 2 eV are also detected. BEEM imaging reveals domains whose edges follow the surface grain boundaries. Modifications of the metal work function and the behavior of interfaces as metal-insulator-semiconductor (MIS) structures are invoked to account for these observations. This also demonstrates the extreme sensitivity of the barrier height to the stoichiometry of the ZnSe at the interface.

EXPERIMENTAL DETAILS

BEEM experiments have been performed on a homemade pocket-size STM already described elsewhere.[14] For ballistic-electron-emission spectroscopy (BEES), a specific electronic setup provides a variable bias voltage between tip and sample, and detects the induced collector current variations with a resolution in the picoampere range. The threshold, beyond which a ballistic current appears in the semiconductor, gives the Schottky-barrier height. Each spectra sequence is then stored in a computer for further processing.

The Schottky-barrier height is deduced from each spectrum by fitting the experimental values with the formula given by Kaiser and Bell[3] for the ballistic current which gives an accuracy within ±0.05 eV. The number of carriers which overcome the potential step is then related to two parameters: $\phi_b = eV_b$, the Schottky barrier height and R (in eV^{-1}), a constant which measures the attenuation due to scattering in the metal overlayer.

For BEEM imaging, the bias voltage is kept constant above the threshold V_b. While the STM tip is scanning the gold surface, the current variations in the semiconductor are used to probe the interface. Because of the low ballistic currents detected on these Au/n-ZnSe junctions, tunneling currents of 20 nA are routinely used in order to increase the signal-to-noise ratio. For the same reasons and because unexpectedly high threshold values (>2 eV) are obtained, bias voltages of 2.5 V are necessary. It should be taken into account that the contrast in BEEM imaging is not necessarily related to the local Schottky-barrier height but is strongly dependent on the diffusion of the electrons during the ballistic transport in the metal. From a spectroscopic point of view, the contrast is mainly due to different slopes of each spectrum rather than to different thresholds.

Samples consist of iodine-doped n-type ZnSe films grown by molecular-beam epitaxy (MBE) on (100) n^+-GaAs wafers (carrier concentration 5.10^{18} cm^{-3}). Their thickness and carrier concentration are 3 μm and about 10^{16} cm^{-3}, respectively. Previous x-ray-diffraction experiments have demonstrated the orientation of these epilayers to be along [100] directions.[15] For electrical characterization of Au/ZnSe interfaces, the epilayers of n-ZnSe were etched in a solution containing 0.5 g of NaOH and 0.5 g of $Na_2S_2O_3$ in 100-ml H_2O. Two or three minutes etch in this solution at 80 °C produces shiny surfaces suitable for fabrication of electrical contacts. X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES) studies show that these surfaces are slightly rich in Zn but very close to stoichiometry.[15]

After this etch, Au films are deposited with a thickness of 15 nm through circular masks, 0.5 mm in diameter in a vacuum of about 10^{-6} torr. An electrical contact is made before each BEEM observation by bonding a small 50-μm-diameter copper wire on a border of the Au film. A thick In layer, use to hold the n^+-GaAs substrate during MBE growth, served as the back ohmic contact for measuring current transport across the structure and ballistic current. A diagram of the experimental setup is shown in Fig. 1. Current-voltage characteristics were measured and analyzed using a fully automated (I-V) system with a Keithley 619 electrometer and a Keithley 230 voltage source.

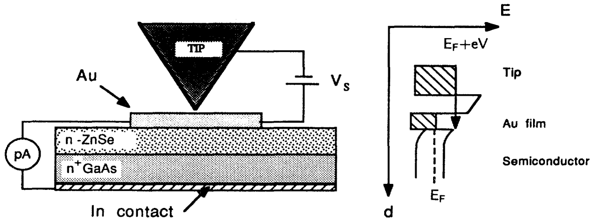


FIG. 1. Schematic diagram of the experimental setup showing the polarization of the n-ZnSe epilayer and the detection of the ballistic current through an In ohmic contact realized on the back of the n^+-GaAs substrate. The drawing on the right gives the energy band diagram when $V_s > \phi_b$.

RESULTS

The current-voltage measurements of the electrical characteristics of the Au/n-ZnSe contacts fabricated on nearly stoichiometric ZnSe surfaces show the formation of a large Schottky barrier at this interface. Some contacts have produced very large Schottky barriers of $\phi_b = 1.67 \pm 0.02$ eV with ideality factors close to unity ($n < 1.17$). A forward I-V characteristic of one such diode is presented in Fig. 2. The reverse current is below the measuring capabilities of the measurement system. However, for different diodes prepared in separate batches, the barrier heights spread in the region of 1.65±0.04 eV. It is also repeatedly noted that some contacts prepared during the same process produced barrier heights of $\phi_b = 1.48 \pm 0.02$ eV, with a very similar ideality factor of $n < 1.18$.

In Fig. 3, characteristic BEEM spectra are presented. They show the variations of the collector current in terms of tip-sample bias voltage. It should be noted that this type of result is obtained in a very reproducible way on all the samples tested. These three spectra are characterized by three different thresholds: spectrum (a) yields a ballistic current above 1.5 V. For spectra (b) and (c), this threshold is about 1.8 and 2.1 V, respectively. The collector current in spectrum (a) is below 15 pA, which is relatively small when compared with Au/n-Si contacts. Such collector currents are observed for tunneling currents in the nanoampere range in the latter case, while for these Au/n-ZnSe junctions the weakest injected currents should exceed 15 nA.

A tendency toward saturation at relatively high voltages is also evidenced in the spectrum (a). This effect has already been observed in a large number of BEEM experiments, and underlines the importance played by the variations of the electron mean free path in terms of incident

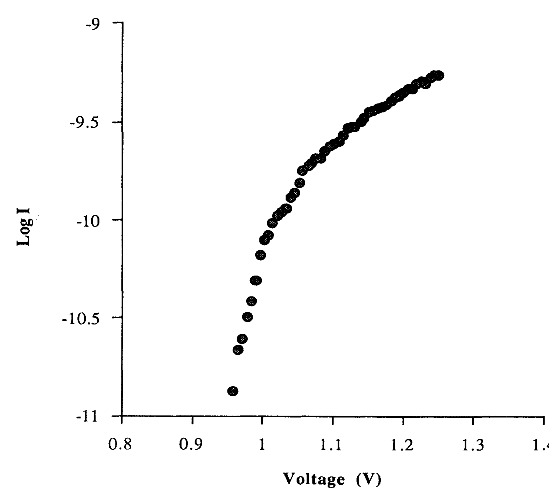


FIG. 2. Forward [ln(I)-V] characteristic of a Au/n-ZnSe contact giving a Schottky-barrier height of 1.67 eV with an ideality factor of $n = 1.05$.

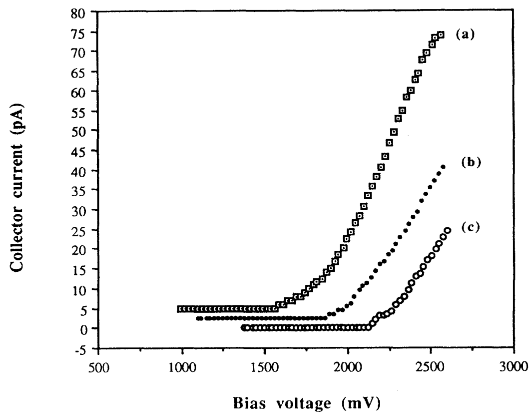


FIG. 3. Ballistic current as a function of sample bias voltage for three different tip positions giving three characteristic thresholds. Fitting by the Kaiser and Bell formula gives, respectively, (a) $V_b=1.64$ V, $R=0.00091$ eV^{-1}; (b) $V_b=1.83$ V, $R=0.0009$ eV^{-1}; and (c) $V_b=2$ V, $R=0.00078$ eV^{-1} (R is the attenuation factor due to scattering).

energy.

Contrary to Au/Si or Au/GaAs junctions, where almost all the interface gives a significant ballistic current, these samples are characterized by very small active areas, a few tens of nanometer square in diameter over a total area of 0.04 μm^2 which is the maximum area attainable with our STM. Therefore, a spatial analysis of the barrier height variations, as presented in the work of Fowell *et al.*,[13] is often impossible. Nevertheless, a distribution has been established by moving the sample with the electromagnetic louse several micrometers apart, and by probing the local barrier heights. This distribution is presented in Fig. 4. It is shown that the Schottky-barrier height ranges from 1.53 to 2.15 eV. Moreover, the distribution is highly asymmetric with a maximum around 1.65 eV and a tail toward higher values.

These local effects may be also studied by BEEM imaging. Figure 5(a) shows the surface topography (left) and the ballistic current variations (right). The scanned surface is 40×40 nm^2, while the bias voltage is kept constant at a value of 2.5 V. The gray scale levels give the roughness of the gold epilayer (15 nm from black to white) or the collector current (from 0 to 25 pA). The STM images yield the topography of the gold surface with characteristic grains several nanometers in diameter. The ballistic images shows a very localized emissive area (7.5×12.5 nm^2). When compared with the topography, it appears that this domain corresponds to a surface grain. A spectrum has been obtained on the active area and is presented in Fig. 5(b). This spectrum gives a threshold of 2.10 eV with an R parameter of 0.0018 eV^{-1} (full line).

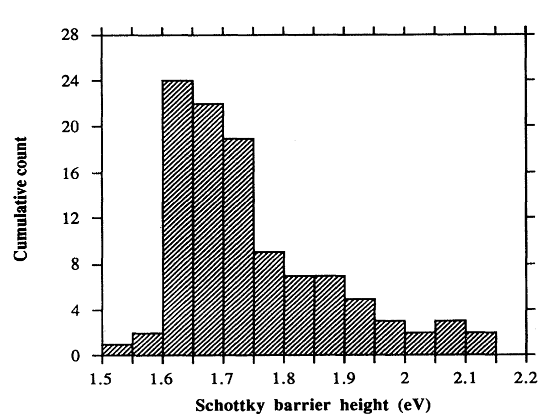


FIG. 4. Histogram of the Schottky barrier heights deduced from more than 100 BEEM spectra taken on several contacts. This wide distribution presents a maximum at about 1.65 eV. Unexpectedly, thresholds beyond 2 eV are also observed.

A second example is presented in Fig. 6(a). In this case, the BEEM domains include several gold grains. The ballistic current inside these domains is sometimes irregular and forms subdomains, a few nanometers in diameter. Figure 6(b) shows a spectrum taken on the more emissive area of Fig. 6(a). The fitting curve using the Kaiser and Bell formalism gives $V_b=1.78$ V and $R=0.0027$ eV^{-1}. Other spectra taken on the same domain show that the only varying parameter is R, while the calculated threshold is found to be constant.

DISCUSSION

Because of its optical properties in blue-green light-emitting devices, ZnSe and metal/ZnSe contacts have been widely studied. The first papers on this II-VI compound demonstrated that the barrier height of the metal/ZnSe contacts may be, in a first approximation, explained by the Schottky model ($\phi_b=\phi_m-\chi$, where ϕ_m is the metal work function and χ is the electronegativity of the semiconductor) contrary to group-IV and III-V semiconductors, where the Fermi-level pinning is due either to defect states[16] or to metal-induced-gap states (MIGS)[17,18] and is less dependent on the metal used. For example, Nedeoglo, Lam, and Simashkevich[19] found a linear relation between the Schottky-barrier height and the metal work function: $\phi_b=0.42\phi_m-0.63$, while Tyagi and Arora[20] approximated their experimental data by the following formula: $\phi_b=0.56\phi_m-1.27$. Later experiments using photoelectron spectroscopy confirmed this tendency.[21–24] In this literature, the experimental values generally deduced from I-V or C-V techniques on Au/n-ZnSe contacts range from 1.37 to 1.65 eV.[19–27] This large disparity of the data for the same metal may be explained with difficulty by the Schottky model, which is therefore relatively approximative and only gives a tendency for the barrier height.

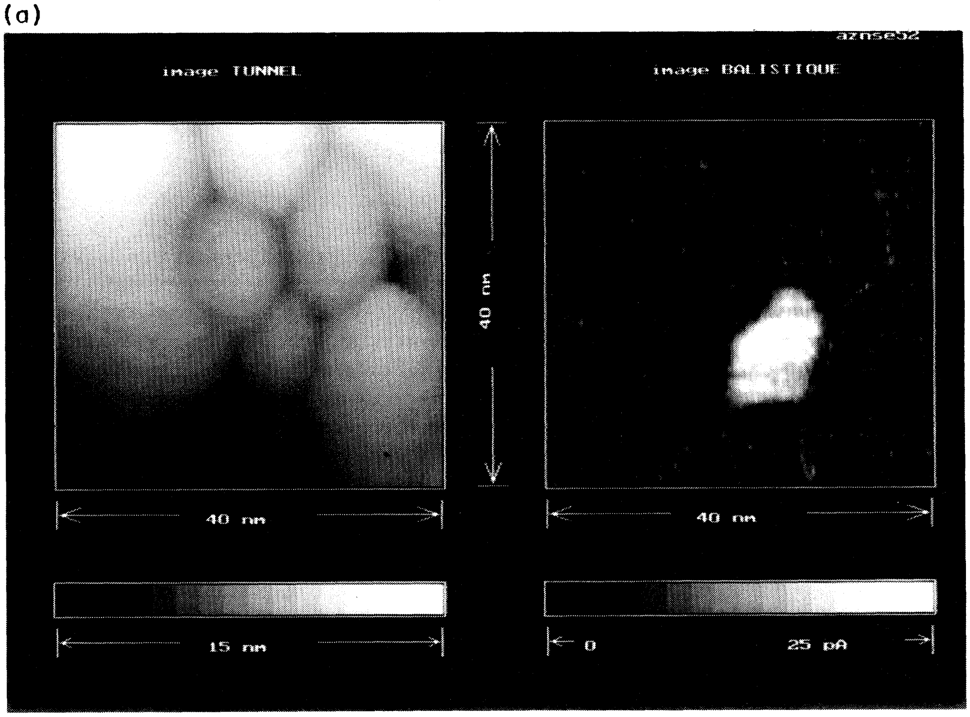
The I-V characteristics of these samples yield Schottky-barrier heights in good agreement with previous work. For example, the I-V characteristic shown in Fig. 2 gives a barrier height of 1.67 ± 0.02 eV, comparable to the value previously reported by Tarricone[25] ($\phi_b=1.65$ eV). The lower barrier heights, 1.48 eV, observed in this work again agree well with the Schottky-barrier height reported by Tyagi and Arora[20] ($\phi_b=1.47$ eV) and Nedeoglo, Lam, and Simashkevich[19] ($\phi_b=1.49$ eV). These different barrier heights for the Au/n-ZnSe system indicate that these contacts behave in a manner similar to metal/n-CdTe systems.[28]

BEEM experiments confirm this hypothesis. The histogram of the data (Fig. 4) indicates that the spread is still enhanced and extends toward large values (from 1.53 to 2.15 eV). As BEEM experiments have been performed on several contacts, relatively small values ($\approx$1.55 eV) correspond to junctions where the smallest macroscopic Schottky-barrier heights have been obtained ($\phi_b = 1.48$ eV). The difference between the macroscopic and the smallest microscopic values is due to the exponential dependence of the thermionic emission current involved in this process. The thermionic current therefore flows through the lower Schottky-barrier height domains, while BEEM current concerns only a given area at the interface. Moreover, the maximum of the distribution ($\approx$1.65 eV) is in perfect agreement with the I-V results, and suggests that this threshold is the most probable among the studied contacts.

The large Schottky-barrier height values deduced from the BEEM spectra may indicate that the Au/n-ZnSe junction does not locally present an abrupt interface with a well-defined metal-semiconductor boundary. Following the analogy with the BEEM results on Au/n-CdTe contacts and the work of Freeouf and Woodall,[29] the model of the effective work function can be tentatively used to explain these observations. This model suggests that the Fermi level is related to the work function of microclusters at the interface, each of them having its own work function. The "ideal" Schottky model therefore becomes $\phi_b = \phi_{\text{eff}} - \chi$, where ϕ_{eff} is the average of the work functions of different interface phases. For most of the semiconductors, it is shown that the effective work function is due mainly to the work function of the anion: ϕ_{Anion}.[29]

If the Freeouf and Woodall model is applied to this system, one obtains $\phi_{\text{Anion}} = \phi_{\text{Se}} = 5.68$ eV.[30] Taking the

(a)



(b)

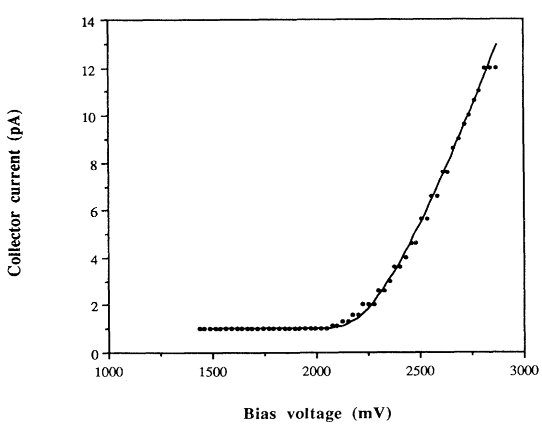


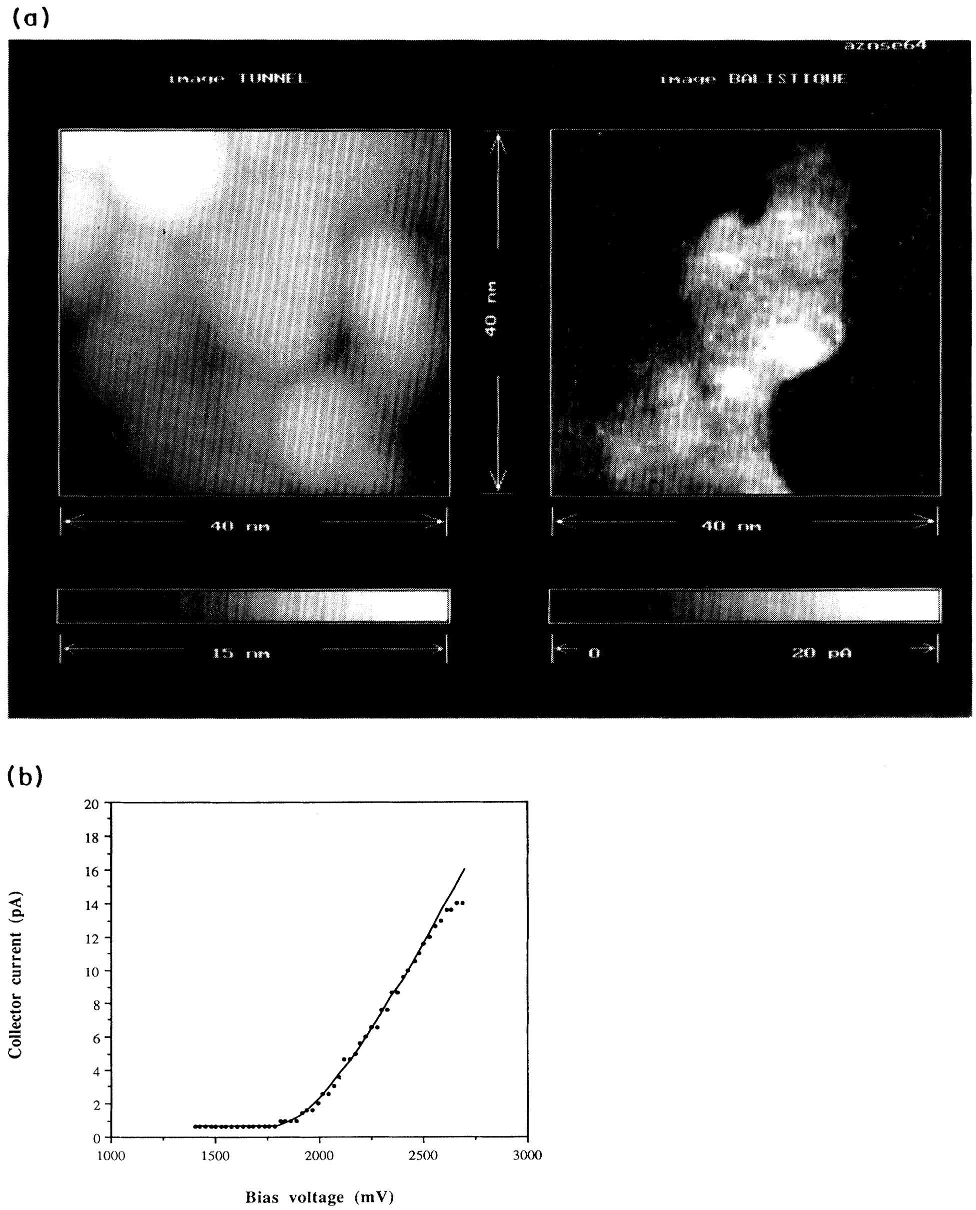
FIG. 5. (a) STM topography (left) and BEEM image (right) of the Schottky junction. The scanned surface is 40×40 nm^2 ($I_{\text{tunnel}} = 25$ nA, $V_s = 2.5$ V). The maximum contrast of the BEEM image corresponds to collector current variations of 25 pA. (b) Experimental BEEM spectrum realized on the bright area of (a). The calculations yield a Schottky-barrier height of 2.10 eV (solid line).

previous remarks on the Schottky model into account, the barrier height is then given by $\phi_b=\phi_{Se}-\chi=5.68-3.51=2.17$ eV, which is in good agreement with the maximum experimental values of ϕ_b: 2.15 eV (see Figs. 3 and 4). Depending on the nature of the complex at the interface, the local Schottky-barrier height might vary from the "theoretical" value ($\approx\phi_m-\chi=1.59$ eV for polycrystalline gold) to the "effective" one ($\approx\phi_{eff}-\chi=2.17$ eV).

On the other hand, the results can equally be explained in terms of Fermi-level pinning at the peak value of 1.67 ± 0.02 eV, below the conduction band. The asymmetric tailing toward the high barrier heights can arise due to the behavior of interfaces similar to localized MIS structures. Microclusters such as Se, native oxides, or any other phases may act as the insulating layer to vary the barrier height only to higher values.

Another possible interpretation may be to consider the different orientations of the gold grains and to take the work function of each orientation into account: $\phi_{Au(100)}=5.47$, eV, $\phi_{Au(110)}=5.37$ eV, and $\phi_{Au(111)}=5.31$ eV.[31] But in this case, the distribution should be less broad ($\Delta\phi_{Au}=0.16$ eV) and the barrier height should have discrete values corresponding to each orientation.

The different contrasts observed in the BEEM images are more difficult to explain, and are not very dependent on the local barrier height in these experiments. The large areas where ballistic current is undetectable may be attributed to the presence of oxides at the interface. Indeed, previous BEEM experiments performed on Au/Si or Au/CdTe have also shown evidence of such domains, which have been interpreted in terms of thick



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oxide layers at the interface that considerably decrease the transmission probability of the injected electrons. These oxide layers may be formed after chemical etching and prior to the gold deposition. Tarricone[25] reports the presence of a ZnO layer at the Au/n-ZnSe interface but, in this case, low barrier heights ($\approx$0.65 eV) typical of Au/ZnO should be detected for thinner oxide layers.

The maximum injection angle θ_c between the incident electron path and the normal to the interface should also be taken into account. This critical angle explains that only electrons whose injection angle at the interface is less than θ_c enter into the collector. As the critical injection angle is only a few degrees ($\approx 6°$ for V=2.5 V), this could explain that most of the electrons are reflected in the metal overlayer and do not enter into the semiconductor as soon as the interface becomes slightly rough.

However, this cannot fully explain why the ballistic domains correspond to surface gold grains, as shown in Figs. 5(a) and 6(a). This contrast may be due either to interface domains whose edges perfectly follow the grain boundaries, or to effects of the grain orientation on the electron transport. On polycrystalline films, each grain has its own orientation. Depending on this orientation, channeling or, on the contrary, multiple diffusions may occur during electron transport which increases or reduces the electron mean free path and, then, the collector current.

CONCLUSION

Au/n-ZnSe contacts have been studied by ballistic-electron-emission microscopy. The BEEM spectra reveal an unexpectedly large distribution of the Schottky-barrier heights with values ranging from 1.53 to 2.15 eV. The highest incidence at 1.65 eV is in good agreement with values deduced from the macroscopic I-V measurements ($\approx$1.67 eV). Higher barrier heights may be interpreted in terms of microclusters of different phases at the interface. This could be due to changes of the overlayer work function or the behavior of the contact as a MIS structure. The work is at hand to identify the appropriate mechanisms. BEEM images show very localized patches which are supposed to be due to the interface roughness and multiple diffusions of the ballistic carriers in the Au layer.

More generally, BEEM on metal/II-VI semiconductor contacts appears to be fundamental to the understanding of the multiple and still partly unexplained thresholds reported in the literature. As the contacts on II-VI compounds are extremely sensitive to the deposited metal and stoichiometry of the semiconductor at the interface, ballistic-electron-emission-microscopy seems to be one of the most suitable tools to investigate these peculiar Schottky junctions.

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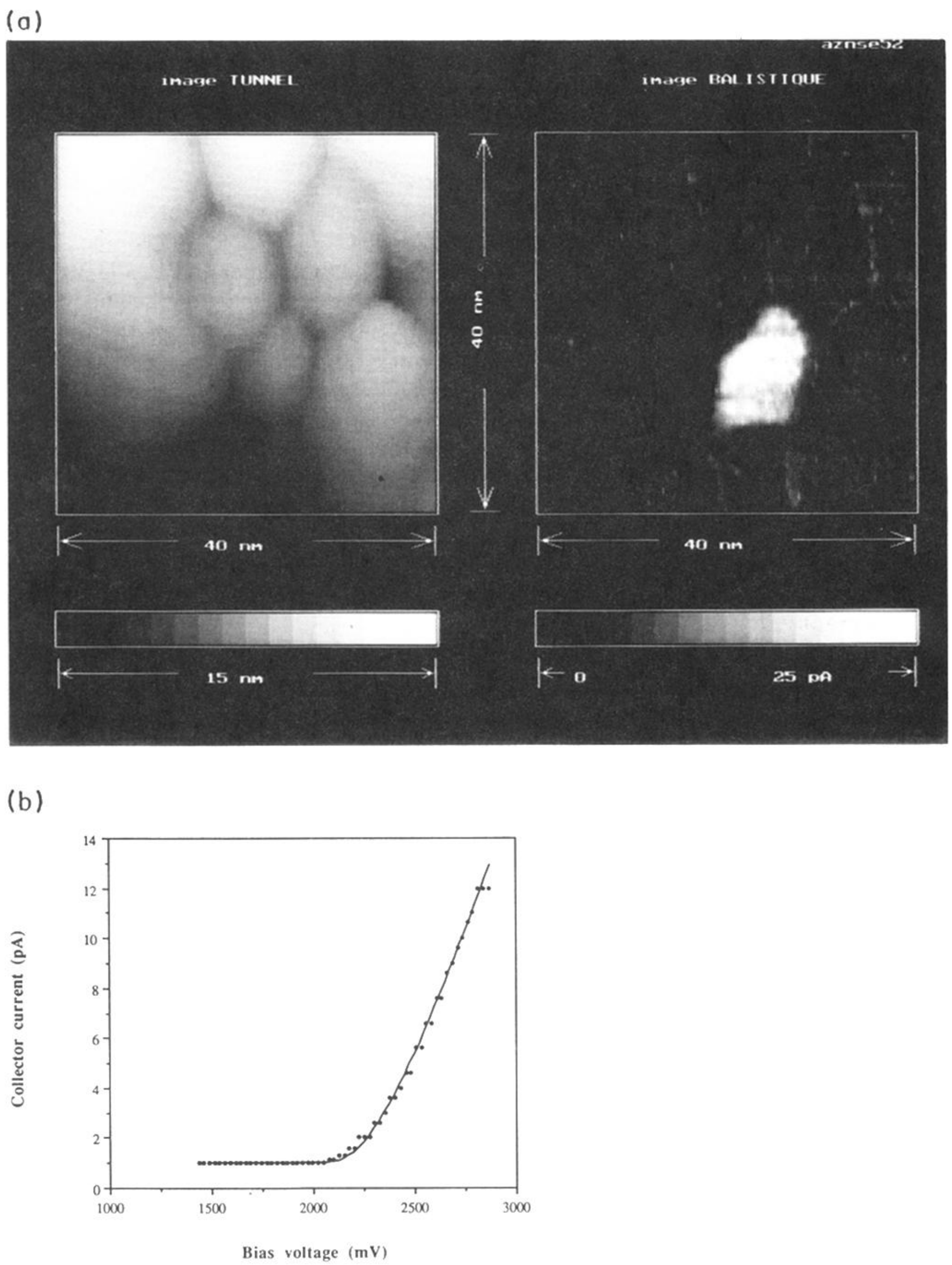

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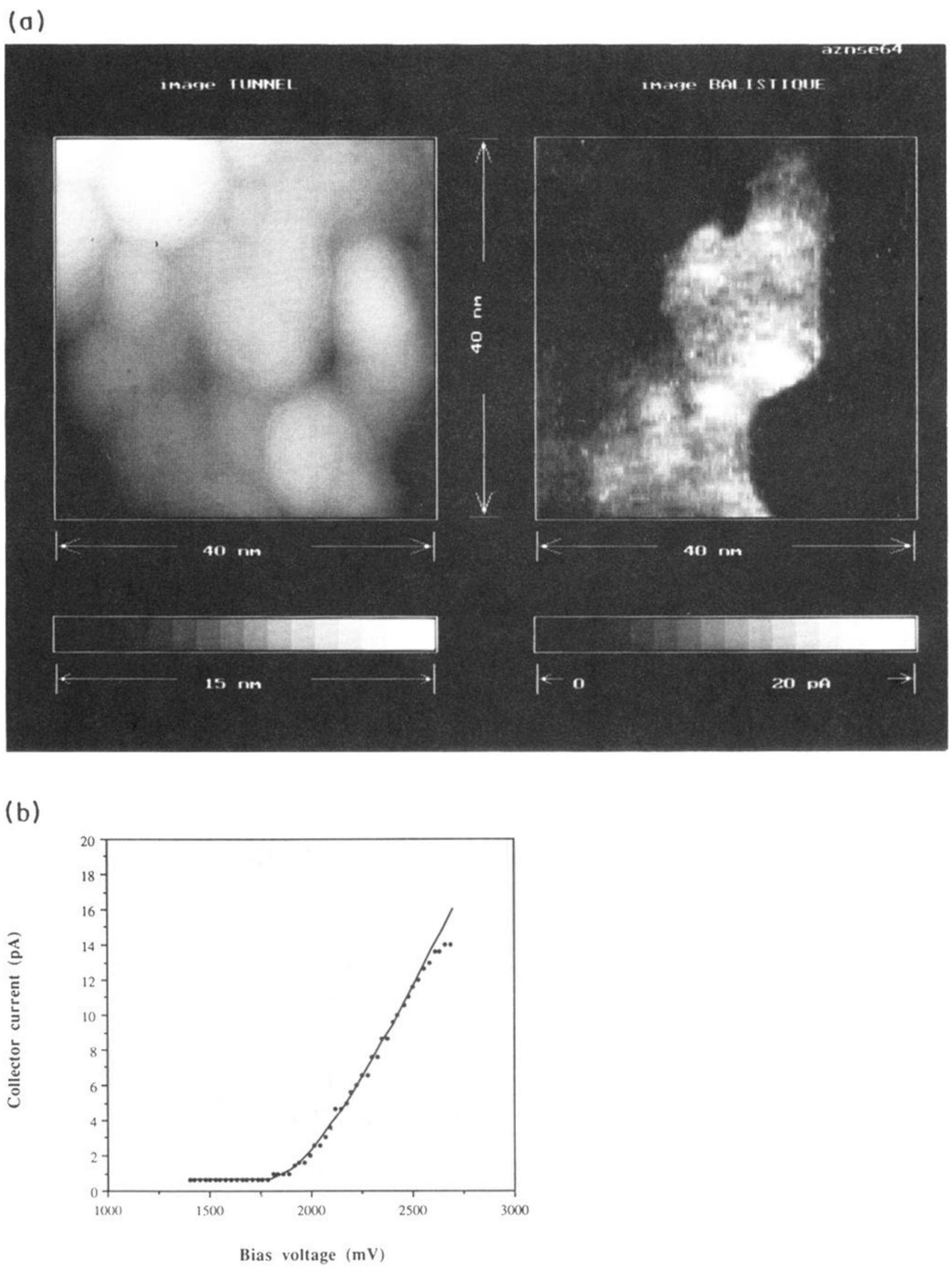

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