

Surface-disorder effects in angle-resolved photoemission spectra

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We report for the first time the evidence of a strong correlation between angle-resolved photoemission spectra and surface disorder. This was observed for the case of cleaved GaAs(110). While for well-ordered surfaces a direct-transition model is clearly the dominant process, in the case of surfaces with a high density of random steps the photoemission process switches to a one-dimensional density-of-states regime. In both cases the spectra are still interpretable in terms of bulk band emission along the crystal normal. These results may explain the behavior of some materials, such as the IV-VI compounds, whose spectra do not seem to follow the direct-transition model.

INTRODUCTION

The problem of surface defects in photoemission is twofold, as defects can both introduce new states¹ and influence the spectrum itself.² We will focus the discussion on the latter point. The effect of surface imperfections on photoemission spectra in general and angle-resolved photoemission spectra (ARPES) in particular has received sparse attention at best despite the fact that the surfaces normally encountered in experiments are not always ideal. By "nonideal" we refer to the surfaces which depart significantly from the ideal two-dimensional termination of the solid due to the presence of surface defects such as steps, vacancies, facets, etc. (we are not including surface reconstruction in this discussion). These defects are found most often on the cleaved surfaces of semiconductors, although they can also be introduced, for example, by chemisorption processes, on metal surfaces too. These surface defects have instead received wide attention in low-energy electron diffraction (LEED).^{3,4} It is the aim of this report to associate some anomalous photoemission spectra from gallium arsenide surfaces with the presence of such defects.

Surprisingly, photoemission spectra completely interpretable in terms of bulk \vec{k} -conserving transitions⁵ can be substantially altered if a large concentration of surface defects is present to the point that the dominant mechanism of the photoemission process is switched from the direct-transition regime to the one-dimensional density-of-states regime. The spectra still reflect the bulk three-dimensional band structure, albeit in a completely different appearance.

No evidence of new electron states due to the presence of defects was found in the spectra; this means either that the density of these states was low or that the amplitude for emission in the normal was much smaller than the bulk emission in that direction.

EXPERIMENTAL

The data have been collected at the Synchrotron Radiation Center, University of Wisconsin—Madison Stoughton, Wisconsin, using the radiation emitted by the storage ring Tantalus 1. The details of the analyzer, a modified cylindrical mirror analyzer, have been published elsewhere.⁶ The experiments were performed on single crystals of GaAs and InSb in the shape of square bars, $0.4 \times 0.4 \times 2$ cm³, the smaller face being parallel to the (110) plane. The samples were Zn-doped⁷ (p type) and chemically cleaned before mounting in a copper sample holder. The effects described in the rest of the paper have been observed on about six different cleaves for InSb and two for GaAs (in the following we will discuss only the GaAs case due to the very well-known behavior of this material; the same interpretations apply to the case of InSb). The samples were cleaved by means of a blade-anvil arrangement where a sharp steel edge was pressed onto the sample side until the cleavage occurred. The other side of the sample was resting against an annealed copper anvil. Two different blade-anvil configurations were used and the resulting spectra showed a very strong correlation with the method employed, as shown in Figs. 1 and 2. In a qualitative sense, the main difference between the two methods of cleaving is that in the first case the stress of the wedge is applied mostly to the fly-off piece, while in the second it is the piece held in the manipulator that is the most stressed. The stress is not equally distributed between the two parts of the crystal, so that we can expect the two surfaces to adjust differently to the cleaving. In many cases, as for silicon, the achievement of a high-quality surface is strongly determined by the cleaving geometry. Less information exists for GaAs, except for the well-known easier cleavability of the III-V compounds as compared to the elemental semiconductors. It is important to stress that both methods gave "good"

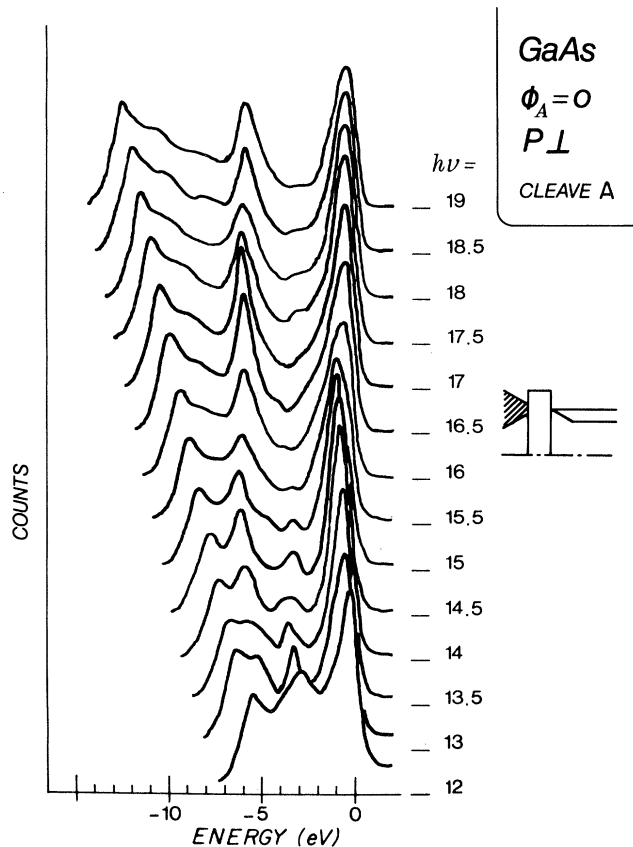


FIG. 1. NE AREDC's from GaAs(110), cleave *A*. Inset refers to the system geometry (see text); also shown is the cleaving-tool orientation.

cleaves, judged from a cosmetic point of view, with large regions of smooth and mirrorlike aspects; a cosmetic point of view is often the only criterion used to assess cleave quality.

Figure 1 shows the normal-emission angle-resolved energy-distribution curves (NE AREDC's) collected from cleave *A*; the radiation was illuminating the sample at an angle of $\sim 50^\circ$ from the normal and the \vec{A} vector was parallel to the mirror plane. The most evident feature of these spectra is the complete absence of dispersion of the peaks with photon energy. In contrast, Fig. 2 shows the spectra collected from cleave *B*, which show the usual behavior of "normal" GaAs, with many spectral features strongly dispersing with photon energy. It has to be stressed that both sets of data were obtained from the *same* sample, the only difference being the cleaving-tool orientation. The surfaces were checked using reflection electron diffraction (RED), performed at 3 keV primary energy, and LEED. A good correlation between the cleaving arrangement and the result was again found: On *A* cleaves the RED pattern never showed any streaks, which are typical of a well-ordered surface, but only the sharp spots lying along the diffraction circles of the three-dimensional crystal, while *B* cleaves regularly showed well-developed streaks. The LEED case was less clear cut as *in both cases* the rectangular pattern typical of the (110) surfaces of GaAs was observed; however, in the case of *A*

cleaves, the spots were somewhat less clear and with a higher background. No quantitative pattern evaluation was available.

Some of the samples were also examined, after removal from the system with a scanning electron microscope at moderate resolution ($0.5 \mu\text{m}$). The surfaces appeared smooth and mirrorlike, aside from a few "tear marks" several micrometers thick spreading across the surface. These structures are always present even on the best cleaves and do not influence the results unless their number is very high as in the case of a "broken" sample, as they are macroscopic features on the scale of surface physics.

To summarize the experimental data, we found a strong correlation between the cleaving technique used and the photoemission spectra obtained. Electron-diffraction techniques further correlate this observation with the surface quality of the sample.

DISCUSSION

Many theoretical models, with various degrees of computational sophistication,⁸⁻¹⁰ for the interpretation of photoemission spectra have been proposed. It is generally agreed that a correct description of the electron final state is the one obtained from a multiple scattering approach, that is the "time-reversed LEED wave function." A full calculation may predict a photoemission spectrum quite well.^{11,12} However, the very interest of ARPES as a spectroscopic technique lies in the possibility of studying the electronic states of the solid; hence the necessity to explain the spectra in terms of the band structure. An important factor in this approach is the availability of accurate band-structure calculations for many materials. From this, then, stems the interest in simplified interpretation models which would allow the analysis of data and the determination of electronic band structures without resorting to full multiple scattering calculations.

Even at this simpler level of interpretation, it is indispensable to relate to a model description of the photoemission process. For example, in almost all the angle-integrated work, it is tacitly assumed that the photoemission measures the total valence-band density of states; this is often done even at low photon energies where this assumption is not generally the case.^{13,14} Things are not so simple for ARPES where the smoothing effect of the angle integration is missing. A simplified "one-step" model has received at least an implicit acceptance and is generally referred to as the "direct-transition" model. We will discuss only the application to the bulk case. If we look to the time reversal of the outgoing plane wave, we see that this state will be made up of a superposition of decaying Bloch states inside the crystal, as is well known from LEED theory.^{15,16} If these states fall in a conduction-band region where the density of states is not zero, they will effectively couple to the solid wave functions.^{8,10} In photoemission, the amplitude for escape in a given direction will then be given by projecting the conduction-band wave function along that direction.^{17,18} The obvious limit of this approach is that the effect of the surface is not taken into account, i.e., the only effect of it is to "filter" out

the Bloch state, forcing the electron into a plane-wave state outside the crystal.^{8,17} This limit applies well in the case of the existence of conduction bands with strong plane-wave components in the detector direction.

In addition to wave functions matching, several other processes are involved in determining the spectrum; the finite linewidth of the spectral structures will be determined by the relaxation time of the system following the creation of the hole. As pointed out by several authors,^{8,11,19,20} two different kinds of broadening mechanisms are active in the photoemission process, namely the hole lifetime and the hot electron lifetime. As the hole-lifetime broadening mechanism will change only the spectral width of the transitions as measured in the AREDC's, it is not of interest here. Hot-electron-lifetime broadening, however, can effectively alter the spectrum itself. The probability of excitation of a valence-band state Ψ_i into the outgoing (exact) wave function Φ_f at the detector may be written^{8,11}

$$N(E, \vec{k}, \hbar\omega) = \sum_i |\langle \Phi_f | \vec{A} \cdot \vec{p} | \psi_i \rangle|^2 \times \delta(E_f - E_i - \hbar\omega) \delta(E - E_f), \quad (1)$$

where the index i (f) refers to the initial (final) states, and the sum extends to all occupied bands; E is the kinetic energy, $\hbar\omega$ is the photon energy, and $\vec{A} \cdot \vec{p}$ is the momentum operator. All the information on the dynamics of the photoemission process is contained in Φ_f .¹¹ In the limit of small broadening this expression reduces to the more familiar form involving Bloch states,^{8,11} which is basically the golden rule of the optical transition with the extra δ on the kinetic energy typical of photoemission formalism; if we disregard the effect of the surface, we can write

$$N(E, \vec{k}, \hbar\omega) = \sum_i |\langle \psi_f | \vec{A} \cdot \vec{p} | \psi_i \rangle|^2 \times \delta(E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega) \delta(E - E_f), \quad (2)$$

where Ψ_f is now a Bloch state. As the transition is now between three-dimensional Bloch states, the conservation of k_{\perp} during the photoexcitation must be preserved. This is then the case of direct transitions, or the so-called limit of "bulk photoemission." Since the matrix element $M_{i,f}$ will be only a modulating factor, we can disregard it and rewrite (2), specializing it to the case of $k_{\parallel}=0$ and making use of the δ -function properties,²⁰

$$N(E, \vec{k}_{\parallel}=0, \hbar\omega) = \sum_{m,i} \frac{\delta(E - E_f)}{\nabla_{k_{\perp}} [E_f(k_{\perp}, m) - E_i(k_{\perp}, m)]}, \quad (3)$$

where the index m refers to the points along the line $\vec{k}_{\parallel}=0$ satisfying the energy conservation. This equation explicitly shows the dependence of the spectral features on the one-dimensional joint density of states, or better its energy distribution through the δ on the kinetic energy.

The important aspect of this equation is its dependence on $\hbar\omega$. For a band structure dispersing with k_{\perp} , this will result in a spectrum showing structures which disperse when the photon energy is changed. The validity of this

approach has been recognized in most cases,^{21,22} but for this discussion we notice only that the spectra of Fig. 2, for cleave B , are fully explainable in this framework.^{5,23}

The other limiting case is that of strong \vec{k} broadening and it can also be worked out from (1). For our purposes, we notice that a full relaxation of the final state k_{\perp} in (3) will directly give

$$N(E, \vec{k}_{\parallel}=0) = \sum_{i,m} \frac{\delta(E - E_f)}{\nabla_{k_{\perp}} E_i(k_{\perp}, m)}, \quad (4)$$

where the dependence on $\hbar\omega$ is now lost and the spectra reflect only the one-dimensional density of (initial) states (ODDOS).²⁴ The spectra generated in these two limiting cases are profoundly different. The spectral features will be stationary at different photon energies and, as the broadening refers only to the "final" state, one will expect fairly sharp features, broadened only by the hole lifetime. This is the same behavior that would be expected from two-dimensional electron states, such as surface states or layered compound valence bands. In the case of three-dimensional solids, this behavior was observed most convincingly for the IV-VI compounds, where the photoemission spectra have been remarkably well interpreted in terms of the ODDOS,²⁴ although it is not clear why the IV-VI materials should set themselves apart from all the other cases, where the direct-transition model explains the data satisfactorily. Another good example, is the case of gap emission, in which the final state corresponds to a region where no conduction-band states are available,^{25,26} the cause is different but again no dispersion is observed as long as the final state is within the forbidden gap.

The off-normal emission spectra are more complex as \vec{k}_{\parallel} changes across the EDC; the general conclusions are, however, unaffected. The formalism will, in this case, be more complex as \vec{k}_{\parallel} is not constant throughout the spectrum anymore, but the general conclusion will still be the same.¹⁰

In the case of our data, the set of EDC's relating to cleave A are clearly not dispersing. Some mechanism must then be active that relaxes the k_{\perp} -selection rule.

We propose that the origin of the anomalous behavior of those GaAs samples is due to a very high density of surface defects, in particular to a distribution of random steps.^{3,4} In other words, the surface is such that atoms and groups of atoms are missing from it, with the other atoms left in their lattice sites, very much similar to a random up-and-down staircase.²⁷ This is *not* a completely disordered surface—some two-dimensional order is left on it. As we will show, this is the only model consistent with all of the data and able to explain the results of Fig. 1.

The RED data indicate strong bulk scattering with a complete absence of streaks on type- A cleaves and well-developed streaks on type- B cleaves; this indicates then the existence of surface defects into which the beam can penetrate and undergo three-dimensional Bragg scattering without being completely absorbed. These defects, however, do not completely destroy the crystal order: If this were the case, only the circles typical of polycrystalline samples would be observed, or, in the extreme case of complete disorder, the RED pattern would be completely

absent. LEED data were consistent with RED data. The LEED data also showed a pattern for type-*A* cleaves, but with a much stronger background and less clear spots than for type-*B* cleaves; also, the LEED pattern vanished into the background above 200 eV primary-beam energy, while it is normally observable up to much higher energies. The studies on the effect of surface disorder on LEED patterns have shown that the LEED pattern itself is not very sensitive to disorder, while the spot shape and size is^{3,4}; for the actual discussion it will be enough to observe that the very existence of the LEED pattern shows that even for a random stepped surface as described above the parallel component of \vec{k} is not fully removed.

Surface facets or macroscopic steps may be ruled out for two reasons: (1) These features are easily distinguished in a LEED or RED pattern, e.g., by the division of the spots in "rosettes,"^{3,4} which were not observed in our case, and (2) macroscopic facets will give spectra equivalent to the sum of the intensity of the spectra originating at the different faces, so than the data should show even more dispersion than the spectrum originating from a single face. If the number of different faces were very high, the spectra would approach the angle-integrated case, with typically broad features, as the photoemission process will then average the intensities coming from the different faces. Our data shows that this is far from being the case,

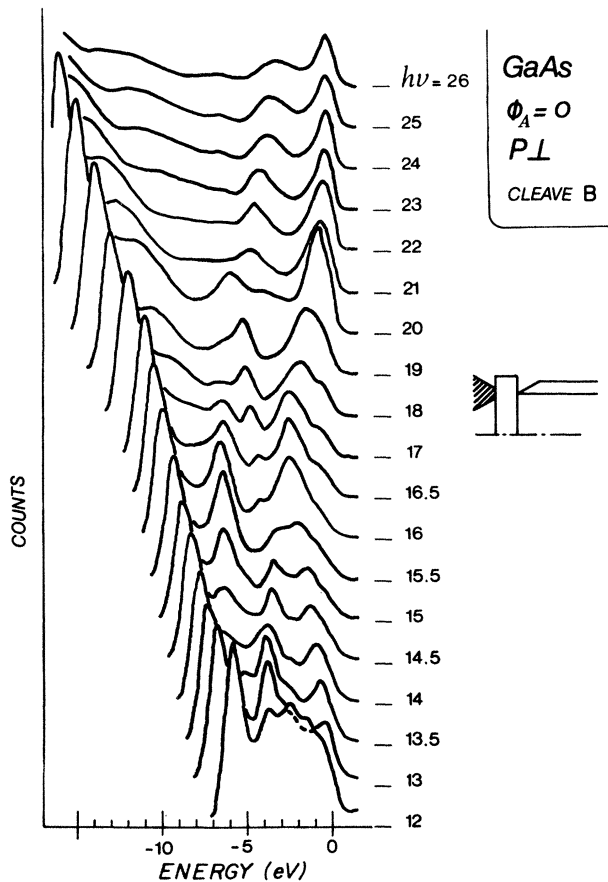


FIG. 2. NE AREDC's from GaAs(110) cleave *B*, under the same experimental conditions.

as the spectral features are too sharp, and again show no dispersion, unlike the angle integrated spectra.^{13,14,23}

On the same basis we can rule out the existence of *ordered* steps onto the surface, as these will be easily distinguished in LEED by the splitting of the spots at particular beam energies.^{3,4}

Summing up the experimental evidence, we believe that the surfaces from *A* cleaves can be described by a random distribution of steps. As is well known from LEED, this does not remove the two-dimensional order but introduces a broadening in \vec{k}_{\parallel} . In addition, our data show that it will cause a random "vertical" disorder which effectively obliterates the perpendicular component of the momentum, giving rise to a regime of nondirect transitions.^{8,11} If this is the case, the spectra should then reflect the ODDOS, as stated before, at least as long as peak positions are concerned. Figure 3 shows just such a ODDOS for GaAs along the (110) direction, courtesy of K.C. Pandey²⁸; the band structure was obtained by an empirical pseudopotential method and broadened by a 0.2 eV Gaussian to simulate the instrumental resolution and compared to one of the experimental EDC's. The structures labeled 1–4 correspond to the top of the valence band (Γ_{15}), X_5 , $(\Sigma_1)_{\min}$, and X_3 , respectively. The agreement in the spectral features' position is indeed striking, proving that what is actually measured on the *A* cleaves is indeed the ODDOS. It is interesting to notice that only bulk features enter in the theoretical ODDOS of Fig. 3, so that no evidence of "defect states" is visible in our data. Owing to the very nature of the experiment this does not exclude that such states would be visible in other directions different from the sample normal.

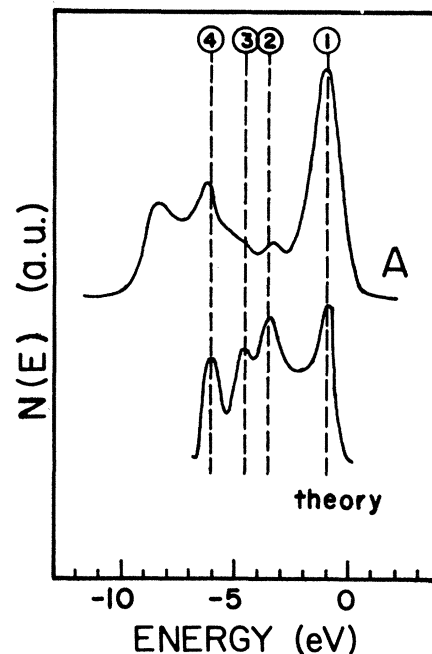


FIG. 3. ODDOS for GaAs along the Σ direction, broadened by a 0.2-eV Gaussian. Upper curve is the NE AREDC spectrum taken at $\hbar\omega=15$ eV from a cleave of type *A*. Structures are discussed in the text.

The above discussion focused on the normal-emission case, $\vec{k}_{\parallel}=0$, as we lack off-normal data. Similar results would, however, apply to off-normal cases, where a full k_{\perp} relaxation would lead to a ODDOS behavior along the reciprocal-space line defined by $k_{\parallel}=\text{const}$. This behavior was observed in the IV-VI-compound case.^{22,24} It is not clear why those materials should set themselves apart from the more general case of direct transition. We conclude that a high density of steps is the likely explanation of the observed behavior. It is well known that the IV-VI compounds are extremely brittle and difficult to handle for that reason²⁸; this may lead very easily to the formation of a large number of microsteps under cleavage that can go undetected in a visual LEED analysis.⁴

CONCLUSIONS

We have shown for the first time the existence of a strong correlation between the *photoemission process* itself and the surface order. While on a well-ordered surface the direct-transition model explains the data in a satisfactory way, the presence of surface defects switches on a ODDOS regime. In other words, the surface disorder give rise to a strong broadening of k_{\perp} , thus effectively removing the \vec{k} -conservation rule typical of the direct-transition model and switching the process to the ODDOS regime.

It then appears that the surface morphology plays a stronger role in determining the photoemission spectra

than was previously suspected, even when the interpretation is in terms of "bulk" photoemission. This result may explain the case of the IV-VI compounds, whose behavior is in striking contrast with the great majority of the other cases. Also, the study of surfaces generated by cleaving might indeed require a more careful assessment of the surface itself before, e.g., comparing electronic DOS's with and without overlayers. This has evident implications for the study of semiconductor surfaces and interfaces with photoemission techniques. From this point of view we want, however, to stress that a surface with random steps is *not* equivalent to an ordered surface with a disordered overlayer, as this will also change the initial DOS, consequently modifying the problem completely. More detailed studies are also needed in order to better understand the onset of the two regimes, in particular a quantitative study of the step density; the extension to metal surfaces will also be interesting.

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