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The influence of surface scattering on photoemission yield spectra in Si(111): consequences for ionization energy determination

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Abstract. Several homogeneous, ordered or disordered, Si(111) surfaces, namely 1×1–H, 7×7–H, $\sqrt{3}$–Ga, $\sqrt{3}$ –Ag and oxygen disordered, have been prepared in ultra-high vacuum and their photoemission yield spectra have been measured in the threshold photon energy range (4–7 eV). As expected along surfaces where the surface state contribution is very small, the spectra obey a power law of the form $(h\nu - E_i)^{\alpha}$, E_i being the ionization energy; α is found to depend strongly on the surface geometry, being two on nearly non-scattering surfaces (the hydrogenated ones) and reaching $\frac{7}{2}$ in a highly scattering case (oxygenated surface) in agreement with theoretical predictions. This leads to an accurate determination of E_i. The validity of this treatment is discussed for surfaces in which the surface state contribution is important.

1. Introduction

The photoemission process from bulk states is well approximated by the three-step model proposed by Spicer in 1958 [1], as supported by several more recent theoretical approaches. After the optical excitation of the electron, in a first step, and its transport toward the surface in a second step, the third step is the escape through the surface. We do not know much about this last step, which appears in photoemission analysis first as a step function with respect to energy and second through the assumed conservation of the electron wave vector component $k_{\parallel}$ parallel to the surface. The latter assumption is essential to translate angular resolved photoemission spectra into band structure terms, but its validity is not definitely established. In the present paper, using accurate high-resolution photoemission yield measurements in the threshold region, we demonstrate that the surface scattering of the photoemitted electron depends strongly on the surface atomic arrangement.

The measurements concerned only Si(111) surfaces of low-doped, low-defect and accurately oriented samples. Various surface atomic arrangements, either ordered or disordered, were prepared by adsorption of the proper amount of different elements (H, Ga, Ag, O). Presumably a common effect of these elements is to remove the surface states that contribute to the photoemission yield spectra in the threshold region. Besides, the work function remains in the same energy range, and therefore the escape depth of the electrons is kept constant. Under these conditions, the first two steps of the photoemission process concerning the upper valence band states are identical for all systems, and the contribution from any other photoemission process, from surface states in particular, is negligible in the photoemission threshold region. Therefore, any difference between photoyield spectra must be the consequence of the escape process through the various surface layers, the thickness of which is never above a few Ångströms.

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2. Experiments

The experimental set-up has been described previously [2]. This ultra-high-vacuum (UHV) system works in the 1×10^{-10} Torr range. It has low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) facilities to check the order and the composition of the surface. The photoyield spectrometer has a calibrated monochromatic source with a very low stray light level and electron collecting optics which allows us to count the photoelectrons from the sample and repel the others. A photon energy range from 4 eV to 6.7 eV was covered and photoyield values as low as 1×10^{-10} electrons per incident photon could be effectively measured.

The sample preparation started with industrial grade Si(111) wafers, 0.5 mm thick, cut into 20×4 mm^2 rectangles. The hydrogenated 1×1 reconstructed surface, denoted Si(111) 1×1–H, was obtained by chemical treatment [3], then loaded and put under UHV as fast as possible, where it underwent photoyield measurements as soon as the pressure was low enough; reconstruction and contamination were checked afterwards by LEED and AES respectively. All the other surfaces were prepared under UHV. The wafer, properly treated before loading, then mounted on the sample holder and put under UHV, was first Joule heated above 900 °C in order to obtain a clean 7×7 reconstructed surface. Then it was either exposed to atomic H, formed by thermal dissociation of H_2 on a Joule heated W ribbon, to obtain the so-called hydrogenated 7×7 reconstructed surface [4], denoted Si(111) 7×7–H, or it was exposed to a flux of Ga or Ag from a calibrated MBE-like graphite crucible, which left on the surface about 0.4 monolayers (ML) of Ga or 1.0 ML of Ag. Upon Joule annealing of the sample at about 450 °C, a $\sqrt{3} \times \sqrt{3}$ R 30° reconstructed surface was obtained, denoted Si(111) $\sqrt{3}$–Ga or Si(111) $\sqrt{3}$–Ag. The actual structure of these two surfaces is not equally well known. Ga is accepted to adsorb in an adatom position, bonded to three surface Si atoms in sites above an Si atom of the second layer [5], giving a saturation coverage at $\frac{1}{3}$ ML. In the case of Ag [6] the actual saturation coverage is above $\frac{2}{3}$ ML and may reach 1 ML; Ag dimers and trimers are probably formed with or without some Si atoms above the Ag plane: there may then be a mixture of two different structures satisfying the $\sqrt{3}$ periodicity and the actual Ag coverage. A disordered surface has been obtained by exposure of the clean Si(111) surface to a dose of 20 Langmuirs of molecular O_2: the 7×7 reconstruction was removed while blurred 1×1 unit mesh remained observable by LEED, meaning that the top two atomic layers were both smoothed and disordered.

3. Results and discussion

A simple theory of photoemission yield in the threshold region for semiconductors was given by Kane [7] in 1962. It assumes that the band bending can be neglected, which is satisfied, in particular, when the doping level is low enough as to render the surface space charge region large compared to the electron escape length. For Si, where the work function is above 4 eV, the doping level must be below about 1×10^{17} cm^{-2}. Kane's theory addresses the present systems and shows that the yield $Y(h\nu)$ can be expressed in the form of a power law

$$Y(h\nu) \propto \left(h\nu - E_{\mathrm{i}}\right)^{\alpha} \tag{1}$$

where E_{i} is the ionization energy. The exponent α can take integer or half-integer values from one to $\frac{7}{2}$ depending on the transition at the origin of the photoelectrons and on the

scattering mechanisms. Si is certainly the semiconductor for which the best fit with this theory can be expected because the valence band density of states at its upper edge is well represented by a parabola over nearly 1 eV [8]: $N(E) \propto \sqrt{E}$, with $E = 0$ at the valence band edge. A clear experimental verification could not be achieved at the time of Kane's theory because the sensitivity of the measurements was not high enough, and discrimination between surface states and bulk state contributions along clean surfaces could not be made. Such a discrimination was attempted many years later [9] with some success on clean surfaces. In the case of Si, correct ionization energy values E_i and densities of surface states comparable to those deduced from angular resolved UV photoemission spectroscopy could be obtained. However, the valence band contribution to the photoyield spectra was not clearly discussed and a power law with an exponent equal to either $\frac{7}{2}$ or $\frac{5}{2}$ was used, leading to some uncertainties in the value of E_i and the density of surface states.

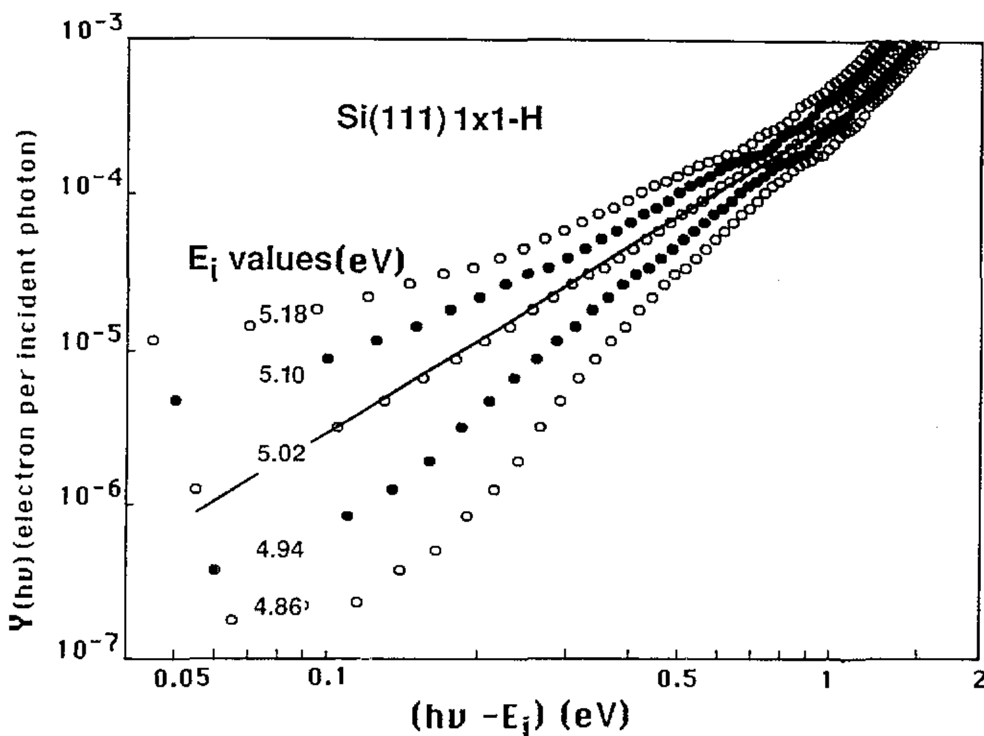

Figure 1. Logarithm of the photoemission yield, in electrons per incident photon, as a function of the logarithm of $(h\nu - E_i)$ for a set of E_i values in the case of an Si(111) 1 × 1–H surface. The straight line represents the function $(h\nu - E_i)^{\alpha}$ calculated with $E_i = 5.02$ eV and $\alpha = 2$, and adjusted to the experimental points plotted with $E_i = 5.02$ eV.

In the present study, an accurate experimental verification of Kane's theory was looked for. No assumption was made about the E_i values. The experimental data, in each case, were a yield spectrum that is a set of yield values $Y(h\nu)$ corresponding to a set of $h\nu$ values. Plotting log $Y(h\nu)$ as a function of log $(h\nu - E_i)$, we looked for the value of E_i which led to the longest straight line. Figure 1 shows such a representation in the case of Si(111) 1 × 1–H: in this plot, one sees clearly that for E_i values above 5.02 eV the measured points are distributed along a curve with a continuously increasing slope while for E_i values below

5.02 eV they are distributed along a curve, the slope of which increases at low $h\nu - E_i$ then decreases at high $h\nu - E_i$. Only for $E_i \simeq 5.02$ eV are they distributed along a straight line, for $0.1 \leqslant h\nu - 5.02 \leqslant 0.9$ eV. This fit with a power law is therefore obtained by eye with sufficient accuracy: it fixes the ionization energy E_i within 0.5% at 5.02 eV for this system. The slope of the corresponding straight line fixes the value of the exponent α in the power law, concerning which no assumption was made in advance: in figure 1, the straight line which fits the experimental data has a slope which is strictly equal to 2.0 (the experimental uncertainty is below ±0.1).

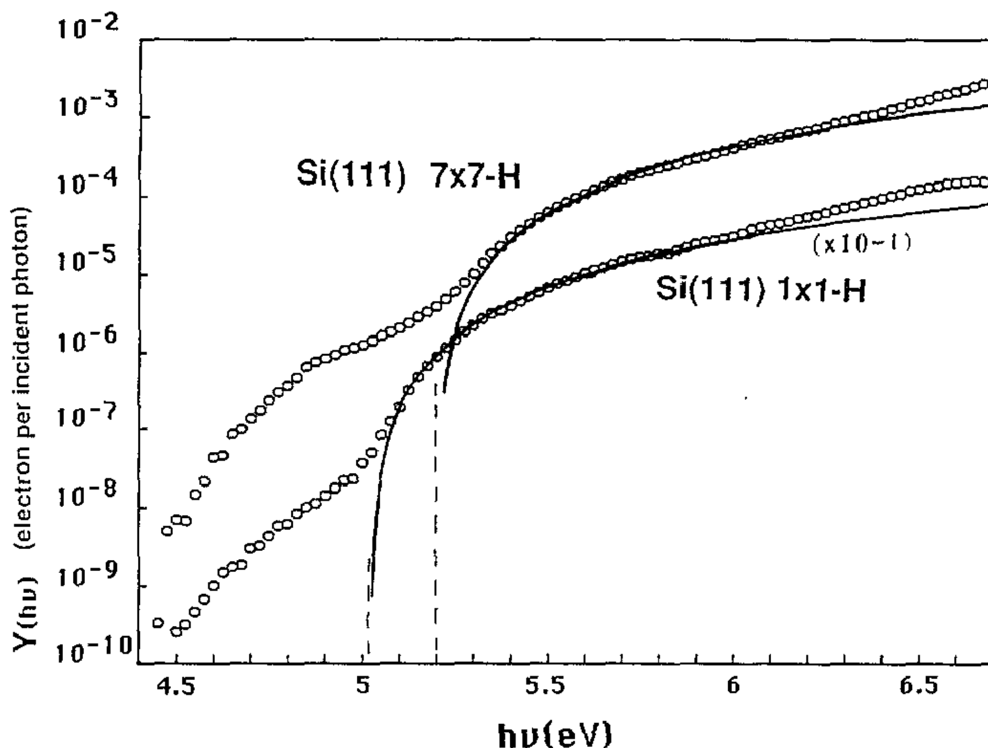

Figure 2. Semilog plot of the measured photoemission yield spectra $Y(h\nu)$ and their best fits with a quadratic power law $(h\nu - E_i)^2$ for an Si(111) 1 × 1–H surface where $E_i = 5.02$ eV and an Si(111) 7 × 7–H surface for which $E_i = 5.2$ eV.

This result agrees very well with Kane's theoretical prediction in the case of direct band to band optical excitation with bulk elastic scattering and without surface scattering. It is quite satisfactory considering the fact that the Si(111) 1 × 1–H structure is the closest to the ideal, unreconstructed (111) surface. The fit covers two orders of magnitude for the yield and close to a 1 eV range from E_i in energy, that is nearly 1 eV into the valence band from the valence band edge, for the initial states. The discrepancy beyond 1 eV is expected from the Si band structure deeper in the valence band. The small discrepancy in the first 0.1 eV from the valence band threshold will be discussed after considering the case of Si(111) 7 × 7–H. For the latter, using the same procedure, one again obtains $\alpha = 2$ while $E_i = 5.2$ eV. The results for the two hydrogenated surfaces are shown in figure 2 where the experimental points and their best fit square laws are drawn, this time using a semilogarithmic plot, allowing us to see the full energy scale. Below E_i at low photon

energy, a tail of states is clearly visible in both cases, more important in the 7 × 7–H case than in the 1 × 1–H one. This tail can be attributed to the remaining surface states in the gap of Si, the chemically treated surface being closer to perfection than the other one. It is clear, particularly in the case of Si(111) 1 × 1–H, that these surface states bring too small a contribution to the yield to alter the determination of E_i and α: in the $h\nu$ region where the fit is made (5.1–6 eV in this case, figure 2) the surface contribution is more than two orders of magnitude smaller than the valence band contribution.

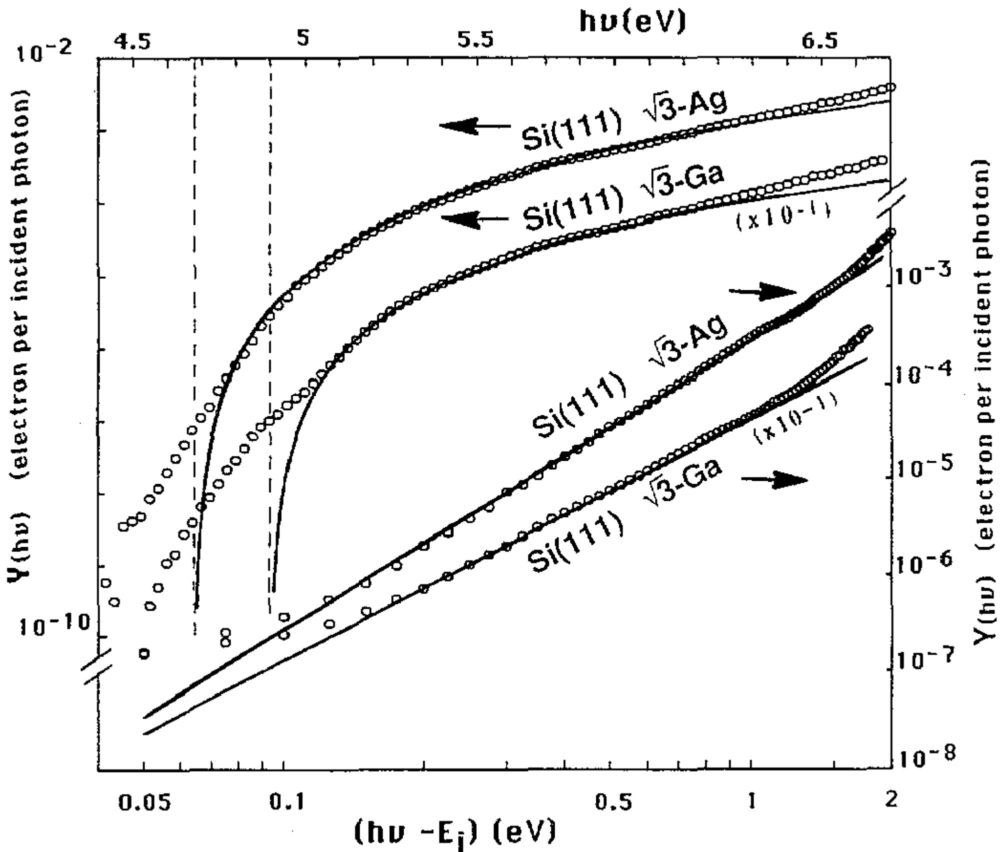

Figure 3. Log–log and semilog plots of the measured photoemission yield spectra $Y(h\nu)$ and their best fits with a power law $(h\nu - E_i)^\alpha$ for an Si(111) $\sqrt{3}$–Ga surface where $E = 4.90$ eV and $\alpha = 2.5$ and an Si(111) $\sqrt{3}$–Ag surface where $E_i = 4.68$ eV and $\alpha = 3$.

Let us consider now the $\sqrt{3} \times \sqrt{3}$ R 30° reconstructed Si(111) surfaces, this periodicity being induced either by $\frac{1}{3}$ ML of Ga or by close to 1 ML of Ag. Figure 3 shows both the log–log and the semilog plots of the two experimental photoyield spectra and the best fit power laws determined in the same way as for Si(111) 1 × 1–H. For Si(111) $\sqrt{3}$–Ga, the ionization energy E_i is found to be 4.90 ± 0.03 eV, which compares well with an earlier determination [10] made from similar data but through a different treatment. The exponent of the power law is found to be $\frac{5}{2}$: this is in agreement with the prediction of Kane's theory [7] when some surface scattering occurs. In the case of Si(111) $\sqrt{3}$–Ag, the ionization energy is even further decreased as compared to the clean surface (5.28 eV) since E_i is

found to be 4.68 ± 0.03 eV, significantly lower than earlier determinations from similar measurements [11], which gave 4.90 eV. Since the work function deduced from the absolute photoemission threshold in the present experiments (figure 3) is close to 4.45 eV, this gives a barrier height $\varphi_b = E_G - (E_i - E_F) = 0.89$ eV. This is higher than the Schottky barrier height deduced from capacitance measurements, which is 0.79 eV [12]. The exponent of the power law is found to be equal to three, which means, following Kane's theory, a stronger surface scattering than in the case of Ga. This excessive surface barrier and this strong surface scattering of the Ag induced structure may very well be explained by a lack of homogeneity along this surface, in which case the E_i value proposed here would have to be taken an as average value.

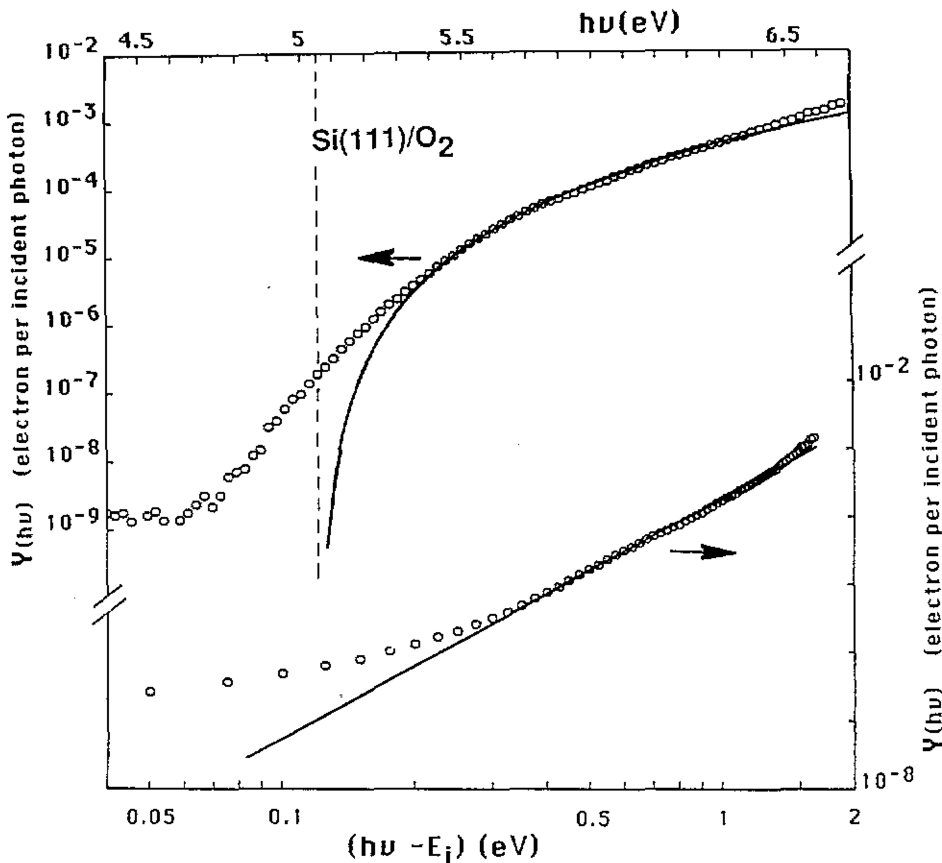

Figure 4. As in figure 3 for an O disordered Si(111) surface: $E_i = 5.05$ eV and $\alpha = 3.5$.

Turning now to the O disordered Si(111) surface, the results for which are presented in figure 4, the ionization energy is found to be 5.05 ± 0.03 eV, and the exponent of the power law $\frac{7}{2}$. This is the maximum value of the exponent in Kane's approach when scattering effects both in the bulk and at the surface are maximized: considering the present case of a fully disordered surface, this is not surprising.

One should note the general quality of the agreement between theory and experiment that has been demonstrated here in at least four different cases; the values of the two parameters E_i and α are physically meaningful. The present approach allows us therefore to appreciate

the degree of order and the scattering effects of the surface from the value of the power law exponent. It also gives a sensitive and accurate determination of the ionization energy in the case, of course, of homogeneous surfaces.

One can wonder now if a similar approach can be applied to the case of surfaces in which surface states contribute more significantly to the photoemission yield spectrum. Past experiments [8] have proved that a risky procedure could be used with some success: in the case of clean surfaces, some information has been obtained on the density of surface states of Si in the valence band edge region, where it dominates the valence band contribution. However the determination of the ionization energy is difficult. In contrast, in cleaved GaAs, the density of surface states at the valence band edge is small, so the ionization energy was easily and accurately determined although the separation of bulk and surface states contributing to the yield was impossible [9]. The present approach is therefore generally limited to surfaces free from filled surface states able to contribute to the yield. In that respect, the adsorption of atomic H at carefully chosen doses may be very useful to test unknown surfaces.

Table 1. Summary of the power law exponents α and ionization energies E_i best accounting for the photoemission yield spectra for various reconstructed Si(111) surfaces.

	Si(111) surface				
	1×1–H	7×7–H	$\sqrt{3}$–Ga	$\sqrt{3}$–Ag	O_2 adsorbed
α	2.0	2.0	2.5	3.0	3.5
E_i (eV)	5.02±0.04	5.20±0.04	4.90±0.04	4.68±0.04	5.05±0.08

In summary we have shown that the surface electron escape in the photoemission process depends strongly on the degree of order and homogeneity of the surface which it has to cross (table 1): line-width and $k_\parallel$ conservation may be significantly affected and this should be taken into account in usual photoemission measurements. Moreover the ionization energy appears as a quantity which is difficult to measure precisely; the few cases where it has been accurately determined here (table 1) demonstrate that its value is hardly predictable for a given system, even when its atomic structure is well known. The present results show that the extrapolation procedure that has to be used depends on the actual surface structure, making direct determination very dangerous when accurate values are needed.

Acknowledgments

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