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Infrared surface absorption in Si(111)2×1 observed with reflectance anisotropy spectroscopy

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Optical transitions between surface states associated with dangling bonds in Si(111)2×1 have been measured by means of reflection anisotropy spectroscopy in the near infrared. The results confirm those previously obtained with other optical techniques (namely surface differential reflectivity and photothermal deflection spectroscopies). The method does not require oxidation of the surface and thus opens the way to studying a number of problems in surface physics, including the temperature dependence of surface transitions in Si(111)2×1 and Ge(111)2×1.

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It is well known that electronic surface states are present on clean surfaces, due to the termination of the periodic potential and/or to atomic reconstruction.[1] The most interesting case is that of semiconductors, where surface states can significantly affect some macroscopic properties like work function, chemisorption, conductance along surface channels, etc.

One of the most extensively studied surface is the cleavage face of Si(111)2×1 (Refs. 2–5, and 7): two bands of surface states separated by a gap are present in the (bulk) forbidden energy gap, on either side of the (surface) Fermi level. They are associated with filled and empty dangling bonds. The theoretical model of buckled π-bonded chains along $[0\bar{1}1]$ directions is now universally accepted.[6,7]

Optical transitions between such surface bands were detected long ago by means of multiple internal reflections and surface differential reflectivity (SDR).[2,8,9] These transitions exhibit a very large anisotropy ($\sim$100%) with principal axes of the surface dielectric tensor along $[0\bar{1}1]$ and $[\bar{2}11]$ directions, i.e., parallel and perpendicular to the chains.[3] A very large anisotropy is also found in Ge(111)2×1.[10,11]

SDR is based on the comparison of reflectivity of a clean surface with that of the same surface when the surface states are destroyed, e.g., by oxidation. Such a differential method, though in general very accurate, has the disadvantage of requiring the oxidation of the surface, an irreversible process that makes the sample unsuitable for a second measurement. SDR cannot then be used to study dynamical processes, phase transitions, etc. In spite of this, temperature dependence of the width and position of the optical peak has been studied in the past with SDR.[4] However, in that work each point referred to a different crystal. This implied a decrease in accuracy (due to a certain sample-to-sample variation of the curve width) and a limited number of points. In addition, measurements at very low temperatures (e.g. liquid helium temperature, LHeT) where oxidation of the surface is very difficult are practically impossible.

The great anisotropy of the optical transitions suggests to perform a RAS (reflection anisotropy spectroscopy) experiment in the near infrared (IR). RAS does not require an oxidation of the surface,[7,12,13] and is then perfectly apt to follow dynamical processes and temperature dependence. The extension of RAS to near IR, though in principle quite simple, poses some experimental problems from a practical point of view.

The RAS signal $S(\hbar\omega)$ is defined as

$$S(\hbar\omega)=\frac{R_\alpha-R_\beta}{\frac{R_\alpha+R_\beta}{2}}=2\,\mathrm{Re}\left(\frac{r_\alpha-r_\beta}{\frac{r_\alpha+r_\beta}{2}}\right), \tag{1}$$

where $R_\alpha(r_\alpha)$ and $R_\beta(r_\beta)$ are the reflectivities (complex Fresnel coefficients) of the sample with light linearly polarized in the α and β directions (in the present case $[0\bar{1}1]$ and $[\bar{2}11]$, respectively[14]). By means of a photoelastic modulator (PEM) it is possible to switch from α to β polarizations and use modulation techniques to increase sensitivity. An accidental anisotropy of the optical system may introduce an unwanted background signal that in principle should be subtracted (see below).

In the present experiment a sample of nearly intrinsic Silicon was cleaved in ultrahigh vacuum (base pressure in the 10^{-11}mbar range) with the double-wedge technique along the $[\bar{2}11]$ direction of the (111) face. It is known that with this technique of cleavage a single-domain surface is very often obtained. *In situ* low-energy electron-diffraction (LEED) analysis was used to check the domain structure of the surface after cleavage.

The optical apparatus is similar to that used for visible and ultraviolet RAS. It consists of a linear polarizer with its axis along the $[0\bar{1}1]$ direction and a PEM that switches the polarization between $[0\bar{1}1]$ and $[\bar{2}11]$ directions. Since the PEM (Hinds Instruments - model 90II/CF57) must be operated at 57 kHz, a fast InSb infrared detector was used, equipped with a sapphire window and cooled to liquid nitrogen temperature. Light entered the vacuum chamber through a $1\frac{1}{2}$'' CaF$_2$ optical window mounted on a home made flange with a Kalrez O-ring. The birefringence-free commercial window[15] is not suitable for IR measurements, being made of standard quartz. A second polarizer rotated by 45° with respect to the first one is put in front of the detector: this defines the direction of polarization of light that enters the detector window and eliminates the effects of its anisotropy. With this expedience any signal due to accidental anisotropy

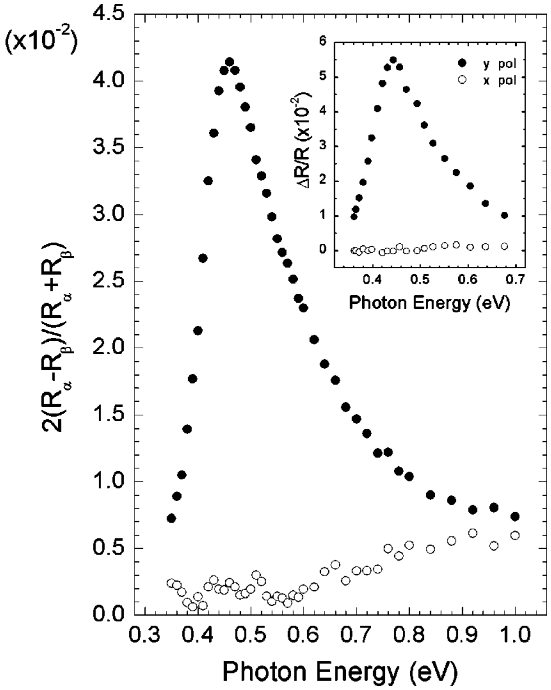

FIG. 1. RAS signal between the directions $[0\bar{1}1]$ and $[\bar{2}11]$ of a Si(111)2×1 surface. Filled (open) circles refer to the clean (oxidised) surface. The inset shows the SDR spectrum of the clean 2×1 surface, obtained in Ref. 3 with light polarized along $[\bar{2}11]$ (x polarization) or $[0\bar{1}1]$ (y polarization) directions.

in the optical system has been reduced to a negligible amount (on the order of 10^{-3}).

Figure 1 shows (filled circles) the RAS spectrum of an (almost) single-domain 2×1 surface ($\sim$80% as shown by the LEED pattern taken immediately after cleavage). To our knowledge this is the first observation of a RAS spectrum in the infrared. The spectrum in the figure is practically the same as that obtained by SDR, as should be expected since the anisotropy of the 2×1 silicon surface is approximately 100% over the entire energy range. The inset of Fig. 1 shows for comparison the SDR spectrum from Ref. 3. The small difference of width between the RAS and SDR curves in Fig. 1 is presumably due to the cleave-to-cleave or sample-to-sample dependence and is present also in previously published spectra.[2,3,9] Closer inspection of the various curves shows that this variance is more frequent in the high-energy side of the spectrum. This suggests that the low-energy-side halfwidth of the peak should preferably be considered in the temperature-dependence studies.

Figure 1 also displays the background signal (open circles) due to residual accidental anisotropies of the optical system. It was taken at the end of the experiment by letting oxygen into the chamber thus destroying the surface states. It is seen that such an unwanted signal is negligibly small. In any case such signal could be subtracted from the main curve, resulting in a small reduction of its width.

All these considerations validate the method of reflection anisotropy spectroscopy in the infrared. On the other hand, the fact that infrared (IR) RAS does not require an oxidation of the surface demonstrate that oxygen does not influence the SDR spectra in this range of energy. The potentialities of the infrared RAS call for a more detailed discussion.

In recent years various theories have pointed out the probable excitonic nature of the optical transitions of Fig. 1.[16,17] In such theories the asymmetric high-energy side of the curve of Fig. 1 is due to transitions to the excited states of the exciton. Measurements at LHeT (not possible with SDR, as already explained) could hopefully resolve possible structures on the high-energy side of the peak.

Theories of the temperature dependence of the width and position of the peak of Fig. 1 are still controversial, and the available experimental data are not sufficient to give an unquestionable answer to this problem. As far as the linewidth is concerned, it is known that *in the bulk* the broadening parameter depends upon the temperature through the Bose-Einstein statistical factor, i.e.,

$$\bar{n}+\frac{1}{2}=\frac{1}{2}\coth\left(\frac{\hbar\omega_q}{2kT}\right), \tag{2}$$

where ω_q is some kind of average of the frequency of the phonons relevant in the optical transitions.[18,19] The expansion of the hyperbolic function yields a linear dependence upon T in the high-temperature limit. The same temperature dependence can also be expected in surface-state transitions if the electron-lattice interaction is weak.[20]

The case of strong electron-lattice interaction has been considered theoretically for the buckled chain model of Si(111)2×1.[21] The width is assumed to depend linearly on the displacement of surface atoms, induced by the TO phonons at $q=0$, that modulates the buckling of the chain. Such displacements are proportional to

$$\sqrt{\bar{n}+\frac{1}{2}}, \tag{3}$$

thus giving a $T^{1/2}$ dependence in the high-temperature limit.[21] A dependence on

$$\coth^{1/2}\left(\frac{\hbar\omega_q}{2kT}\right) \tag{4}$$

is also found in the case of localized transitions,[22] which may be more appropriate to exciton or polaron models.[4,20] Unfortunately the available experimental data on the temperature dependence of the peak width[4] do not allow the discrimination between the existing theoretical models. Measurements at LHeT could hopefully settle the question.[23] Therefore, the infrared RAS measurements as a function of temperature (especially in the low- and high-temperature limits) should shed light on this important problem, and moreover yield an experimental hint to the phonon modes involved in the transition.

In conclusion, we have obtained the near IR-RAS spectrum of a strongly anisotropic surface, single-domain Si(111)2×1 at room temperature. In this way we have demonstrated that reflectance anisotropy spectroscopy, so far used only in the visible—near ultraviolet-range, can be extended to the near-IR region of the spectrum. In future, IR-

RAS could be applied to study many physical problems of clean semiconductor surfaces (excitonic character and temperature dependence of dangling-bond optical transitions in Si(111)2×1 and Ge(111)2×1, surface phase transitions such as Si(111)2×1 to 7×7, etc.). IR-RAS also shows promise in the study of metallic surfaces and possibly other systems, including low-dimensional structures (wires, dots) both metallic and semiconducting.

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