# Observation of Surface States on Ag(100) by Infrared and Visible Electroreflectance Spectroscopy

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By use of the new technique of electroreflectance in the infrared frequency range, a low-lying unoccupied surface state on the (100) single-crystal surface of Ag has been detected. Another absorption feature, due to excitation into a higher surface state, has been seen around 3.1 eV. The positions of the two surface states are in good agreement with the calculated values. A study of the Stark shift of these states has revealed that the electric field near the metal surface has a much more complex structure than hitherto recognized.

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*In situ* reflectance spectroscopy in the visible frequency range has been a valuable tool to detect adsorbed species on the surface of metal electrodes.[1,2] By applying a moderate bias potential (~ 1 V) on the electrode, it is possible to obtain an exceedingly high electric field (~ $10^7$ V/cm) which is concentrated near the metal surface. Inside the metal the field is screened out within a Thomas-Fermi screening length. Therefore, only the surface electronic states are affected by this field. The electroreflectance (ER) experiment, which measures the relative reflectance change of the electrode surface as a function of the potential, should be a very effective method to investigate the surface states of the metal. In absence of specifically adsorbed species and chemical reactions, the ER spectra of (110) surfaces of noble metals often exhibit anisotropic polarization dependence,[3-8] and one possible source of this effect has been shown to be electronic excitations from the filled band states into a band of unoccupied surface states.[9] However, because the experiments were conducted in a narrow range of optical frequency, they could only provide indirect evidence of the existence of the surface states.

In this Letter we report direct observations of two bands of unoccupied surface states on Ag(100) by extending the ER technique from the visible to the infrared frequency range. The positions of these surface states are in good agreement with the calculated values, also reported here for the first time. As expected, the energies of the surface states are very sensitive to the bias potential, and a detailed study of their Stark shifts leads to a new microscopic picture of the electric field distribution in the electrolyte immediately adjacent to the metal surface.

The experiments were performed with silver single-crystal electrodes of (100) surface orientation prepared in the standard manner by chemical polishing.[10] The electrolyte was 0.5*M* NaF made of Suprapur chemicals and triply distilled water. All electrode potentials were measured with respect to the saturated calomel electrode (SCE). The optical measurements were done with linearly polarized light at near-normal incidence. The ER signal $\Delta R/R$, i.e., the relative change in reflectance with potential modulation, was detected by a lock-in amplifier, yielding a sensitivity better than $5 \times 10^{-6}$ in $\Delta R/R$. The signal was recorded at constant wavelength as a function of the electrode potential, which was scanned with 10 mV/sec from $-1.2$ to 0.2 V. The cathodic limit was determined by the hydrogen evolution reaction, and the anodic limit by the silver dissolution. The linear bias-potential scan was modulated by a sinusoidal potential excursion of 180 Hz and of 100-mV peak-to-peak amplitude. For wavelengths longer than 1200 nm a thin-layer cell was used to reduce light absorption in the bulk electrolyte. The sign of $\Delta R/R$ is such that a positive value refers to a reflectance increase with positive going potential.

The ER spectra of Ag(100) for various bias potentials are shown in Fig. 1 for two energy regions where $\Delta R/R$ reveals a weak but distinct structure. The dip in $-\Delta R/R$ is so small that it apparently escaped detection in earlier ER studies in the visible range. Aside from these energy ranges the spectral response is monotonic and structureless, smoothly decaying to zero with increasing wavelength. On top of this smoothly varying positive background, an asymmetric structure with a dip in $-\Delta R/R$ on the low-energy side and a broader positive counterpart is clearly seen, resembling the derivative of a highly asymmetric peak. The most striking feature, however, is the remarkable potential dependence of these newly discovered spectral structures. The position and the line shape for the infrared structure both vary strongly with the applied electrode potential, and the infrared structure disappears as the bias potential becomes more negative than −0.6 V. As has been pointed out in an earlier paper, the strong potential dependence of the spectra suggests the involvement of empty surface states in the optical transition.[9] In this case the zero crossing of our spectral feature would be the most appropriate quantitative measure for the transition energy. Although this position is less well defined than that of the minimum in $-\Delta R/R$ because of the slightly positive background, the uncertainty in the energy values should not exceed about 0.05 eV. Actually, the error incurred in this way causes a systematic shift of the energy to lower values. Hence, in the following the zero crossings are taken as values for the transition energies.

In calculating the energies of the surface states of the Ag(100) we used the self-consistent first-principles pseudopotential method that has been found successful in many surface calculations.[11] The application of this method for Ag(110) has been described in an earlier paper.[9] The Ag(100) surface was investigated by setting up a periodic structure of metal slabs, each seven layers thick, separated by a 12-Å-thick vacuum region. Only the $s$- and $p$-band electrons are iterated to self-consistency. No surface reconstruction or surface relaxation has been observed for the Ag(100), and neither was included in the calculation.

For the charged surface we modeled the external potential by a long-wavelength periodic potential.[9] Upon reaching self-consistency the potential is rapidly screened out inside the metal by an induced charge on the surface layer. We then made contact with the experiments by relating the induced charge to the actual electrode potential through the differential capacitance, which

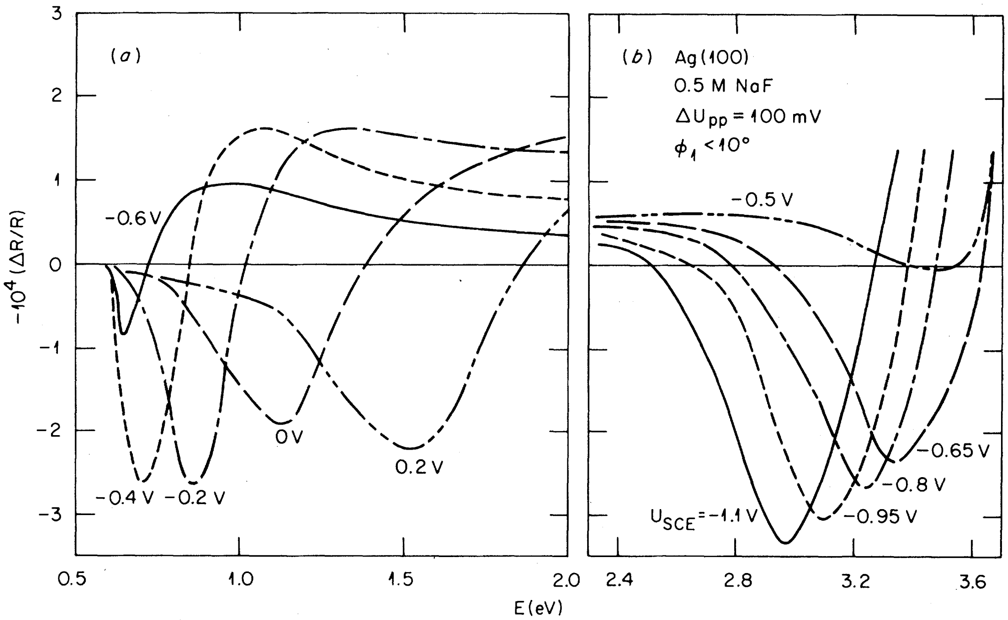

FIG. 1. Electroreflectance spectra of Ag(100) in 0.5 $M$ NaF for various bias potentials and two different photon energy ranges. Modulating potential = 100 mV peak-to-peak. Normal incidence.

was measured independently.

In Fig. 2 we show the surface band structure of the uncharged Ag(100) surface. The corresponding bias potential is the potential of zero charge (pzc), which is $-0.9$ V.[12] The band energies are measured from the Fermi level $E_F$. The large band gap at the point $L$ in the bulk band structure appears at the point $\bar{X}$ of the surface Brillouin zone. In this gap we find two bands of surface states, labeled by $A$ and $B$, respectively. The empty surface band $A$ has $s$ symmetry, and optical absorption can take place by exciting electrons vertically into it from the top of the filled band, which has $p$ symmetry. This results in an absorption feature around 3 eV, which is distinct from the bulk interband edge. The surface band $B$ is mostly occupied at pzc and does not contribute to absorption.

When the surface is positively biased, both surface bands $A$ and $B$ move upward relative to the bulk bands. The upper curve in Fig. 3 shows the good agreement between the calculated and the observed values of the transition energy for a number of bias potentials. At $-0.5$ V of bias the calculated band $A$ merges into the bulk-band continuum and the ER signal is seen to disappear [see Fig. 1(b)]. The bottom of band $B$ is found to move above the Fermi level at $-0.6$ V of bias, and at this point the entire band should contribute to the absorption. Experimentally no ER signal is detectable at $-0.7$ V but a distinct signal is seen at $-0.6$ V [Fig. 1(a)]. However, for band $B$ the energy of the absorption maximum is not simply the energy separation between the surface band and the edge of the projected bulk band. These two states have the same $p$ symmetry at $\bar{X}$ and the optical transition between them is forbidden. To locate the proper initial state we have evaluated the optical matrix elements between the surface states and the filled bulk states and averaged the transition energies weighted by the square of the matrix elements. In this manner the onset of optical absorption of band $B$ is estimated to occur at 0.73 eV, in agreement with the observed value of 0.72 eV. The calculated level shift with the bias potential also compares well with the experiment, including the upturn in the lower curve above $-0.2$ V. The slight discrepancy between the theory and the experiment is partly due to the uncertainties in the differential capacitance measurement.

For both bands of surface states the rate of energy shift with the bias potential is nearly unity. This implies that the potential relative to the bulk metal at the position of the surface state is comparable to the total potential drop across the double layer. This is totally unexpected from the classical theory of electrolyte structure which describes a monotonic drop of potential from the metal surface to the bulk of the electrolyte. Since the surface state is only a small distance $x \sim 1$ Å away from the position of the surface atoms, it should experience only the fraction $x/d$ of the total potential drop, $d$ being the mean thickness of the compact double layer ($d$ should be of the order of 3 Å for the conditions chosen in our experiment). We contend that the unusually large Stark shift of the surface states must

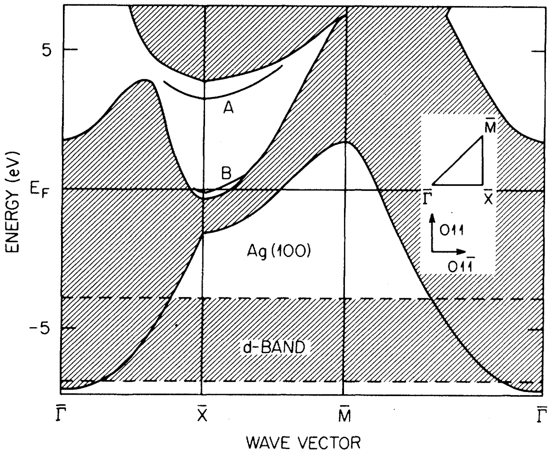

FIG. 2. The Ag(100) projected band structure together with surface states (marked $A$ and $B$). Inset shows the orientation of the surface Brillouin zone with respect to the cubic crystal axes.

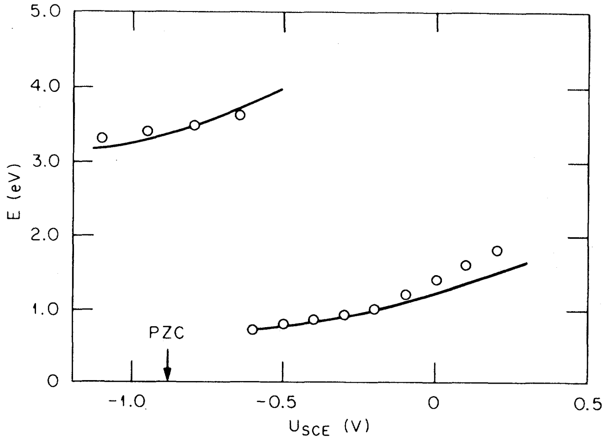

FIG. 3. Shift in transition energies $E$ with bias potential $U_{SCE}$ for excitation into surface bands. Circles, experiment; solid line, theory.

have its origin in the molecular structure of the electrolyte, as was first elucidated by Chan *et al.*[13] These authors analyzed the interaction potential between two hard-sphere ions immersed in a fluid of hard-sphere dipoles. It was found that the interaction potential does not follow the classical inverse distance law but oscillates around the classical potential with a large amplitude. This effect arises from the finite diameter of the dipoles which form alternating shells of overscreened and underscreened regions around each ion. Similarly, at the interface of a metal and a dilute electrolyte the potential near the metal also oscillates around the classical value with a period of the diameter of the water molecule.[14] In the concentrated electrolyte used in our experiment the oscillation should be rapidly damped out by ion screening and only an initial overshooting of the potential remains. This is somewhat analogous to the case of specific adsorption where an overshooting of the potential is also observed. In the latter case the overshooting is caused by charged species held on the metal surface by chemical bonds and counter charge being pulled into the double layer for charge compensation. In the overshooting region where the surface state resides, the local potential can be comparable to the bias potential and the local electric field can be two to three times as high as the average field. We therefore conclude that the electric field distribution in the compact double layer has a far more complex structure than has so far been generally recognized, and we have demonstrated the effective use of surface state measurements to probe this potential distribution.

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