Mapping the Local Density of States by Very-Low-Energy Scanning Electron Microscope

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Reflection of very slow electrons from solid surfaces has been reported to be inversely proportional to the local density of electronic states coupled to the incident electron wave. The reflected electron flux at units of eV used as the image signal in a scanning electron microscope allows mapping of the local density of states at high spatial resolution. Good performance of the microscope at very low energies is enabled by introducing the beam-retarding immersion lens (the cathode lens) with a biased specimen serving as the cathode. Results of demonstration experiments on aluminium are provided. [doi:10.2320/matertrans.MC200921]

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1. Introduction

The local density of electron states (DOS) is an important characteristic of solids. It may also be used to distinguish between different crystal grain orientations in polycrystalline samples or to map dopant distribution in semiconductors.

There are a number of techniques for probing the electron states, most notably (inverse) photoemission. This technique is however hampered by an unreliable knowledge about the upper states involved, that is to say those above the vacuum level (whereas the initial states are practically free-electron-like). The most direct measurement of the states above the vacuum level can be done by inspecting the interaction of very-low-energy electrons (roughly 40 eV and less) with the sample surface.

An electron wave impinging on the sample surface has to transform into electron waves of the crystal periodicity (Bloch states). Its surface-parallel wavevector component k∥ has to be preserved except for the addition of any surface reciprocal-lattice vector,1) which means that the incident electrons may only enter when suitable Bloch states are available and empty. This means that the electron reflection is inversely proportional to the local density of states coupled to the incident wave. It is also due to relative weakness of the absorption potential V⊥ in the incident electron energy range between 0–40 eV that the elastic reflectivity shows a characteristic structure related to the unoccupied band structure E(k). Absorption potential above about 1 eV suffices to suppress any details on the R(E) curve.2,3)

The available techniques are Very-Low-Energy Electron Diffraction (VLEED)2) or measuring the elastic electron reflectivity R(E) where the signal is integrated over the diffracted beams. The inelastic reflected current for these energies and clean surfaces is small and does not vary considerably with energy, so the elastic transmissivity T(E) = 1 − R(E) can be expected to contain the same information.3) The transmissivity can be measured either in the Target Current Spectroscopy4,5) regime (primary-beam-induced current through the sample), or in an imaging transmission mode6) in the case of specially prepared thin samples. The Scanning Low Energy Electron Microscopy (SLEEM)7) however offers the simplest possibility of sequentially imaging the sample in the very-low-energy electron reflectivity regime throughout the whole range of applicable energies, thereby highlighting regions with different DOS above the vacuum level.

1.1 SLEEM and the cathode lens mode

In standard Scanning Electron Microscope (SEM) instruments8) where the energy of the primary beam E remains constant along the optical column, the spot size scales as $E^{-3/4}$. This prevents us to reach low primary electron energies and retain a good resolution at the same time, since only by going down from 10 keV to 1 eV, the spot size goes up by three orders of magnitude.9) Aberration corrected columns allow for smaller spot sizes but the $E^{-3/4}$ energy dependence still holds.

The only way of preserving a small spot size down to an arbitrarily low energy is to use a zero working distance electrostatic lens called the cathode lens (7,9), see Fig. 1). In this mode the beam is kept at a constant energy throughout the optical column and is retarded only at the end of its passage by means of a negatively biased sample. One of the possible cathode lens arrangements is to employ a grounded annular scintillation detector located above the sample which then accelerates the signal electrons onto itself. The spot size scales with energy much more favorably, namely as $E^{-1/4}$, and when certain conditions7) are fulfilled, it can even remain nearly constant.

One more problem solved by electron microscopy at very low energies is the overly large interaction volume of high energy electrons. The information that they provide is no longer quite local, coming as it does from a region up to three orders larger than the illuminated spot itself. Contrary to this, at very low energies of impacting electrons the interaction volume is reduced to a few nanometers’ size, approximately the order of the spot size. The cathode-lens-equipped SEM is therefore a true tool for the nano-world and allows obtaining...
1.2 The aim of this work

This work aims at finding the influence of the density of states in the reflectivity-versus-energy curve of selected polycrystalline and single crystal samples. The influence of surface adsorbates and/or native oxide layers on the expected band structure features in the \( R(E) \) curves is discussed.

2. Experiment

2.1 Experimental setup

Experiments were performed in a Scanning Low Energy Electron Microscope on aluminum samples, both polycrystalline and single crystal ones.

The polycrystalline samples were observed in the Tescan Vega 5130MM scanning electron microscope. This is a standard commercial microscope adjusted for the Scanning Low Energy Electron Microscopy (SLEEM) technique by equipping it with a cathode lens. Its electron gun is of the thermionic emission type and the operating pressure is in the order of \( 10^{-3} \) Pa. At the primary electron energy of 10 keV, the nominal resolution is about 7 nanometers. When the electron beam is retarded to 10 eV by the cathode lens, the spot size grows to some 20 nanometers. The high voltage supply biasing the sample was tunable with a 1 Volt step.

The single crystal samples were observed in an ultra-high-vacuum scanning electron microscope of an in-house design. It has a fully electrostatic optical column by FEI Company and a Schottky type electron gun. The operating pressure in the experimental chamber is of the order of \( 10^{-8} \) Pa. An interconnected preparation chamber permits argon ion sputtering cleaning of the samples in ultra-high-vacuum conditions. The computer-controlled high voltage supply biasing the sample allows for an automated serial acquisition of images with the voltage step of 0.3 Volt. The nominal resolution at 25 keV primary electron energy and low currents is 12 nm. When a 10 keV primary electron beam is retarded to 10 eV by the cathode lens, the spot size grows to 26 nanometers.

2.2 Samples

The polycrystalline aluminum samples were prepared by extruding into a rod, cutting into discs, annealing at 500 °C and quenching in chilled water. The size of the grains was in the order of tens of micrometers. The surface was finished by a conventional electrolytic polishing method in a mixture of perchloric acid and ethanol. These polycrystalline samples were chosen in place of regular rolled metal sheets which proved to be less suitable because of the small differences between grain orientations. The samples were observed “as is”, without any cleaning procedure.

The single crystal aluminum samples with a (100) and (111) orientation were obtained from MaTecK company. The orientation mismatch of the crystal faces was guaranteed to be below 2 degrees. The samples were polished to less than 30 nanometer roughness. Prior to the observation in the ultra high vacuum SEM, each of the samples was in situ cleaned by a 1 keV argon ion sputtering lasting 3 h. For selected experiments, the samples were also electrolytically cleaned in an aqueous mixture of ethyl alcohol, ether and perchloric acid, although this brought in some spurious contamination as a byproduct.

3. Results

3.1 Polycrystalline aluminum samples

The selection from one sequence of SLEEM images of a polycrystalline sample is shown in Fig. 2. In the micrographs, suitable crystal grains were chosen and average signal values were calculated for them in every image of the series. The resulting curve of the reflected signal versus incident electron energy is shown in Fig. 3. The \( R(E) \) curves of the two grains seem to be slightly different in shape but the contrast apparently comes mainly from their being mutually shifted by approximately 0.7 eV, suggesting only the influence of different work functions. The background generated by surface contamination layers may also account for the low contrast level indicated in Fig. 3.

The overall decrease in signal towards the low energy end of the scale is caused by a specific feature of the detection system: the signal electrons coming from the sample are drawn together into a bunch by the electrostatic field between the negatively biased sample and the grounded scintillation detector. This bunch gets narrower as the incident electron energy decreases. For very low energies, this causes a large portion of the signal electrons to escape through the scintillation detector bore, and be lost for detection. The signal decrease with the incident energy is however smooth, monotonical and featureless in itself, since according to Ref. 10) the percentage of lost signal scales as the ratio of primary to incident electron energy. Simple linear baseline subtraction should suffice to highlight the possible density of states (DOS) features in \( R(E) \) without adding unwanted artifacts. It had also been noted by Ref. 3) that \( R(E) \) spectra do not correlate with DOS features in a straightforward way, but in a rather semiquantitative fashion, mirroring band gaps but not necessarily DOS peaks.\(^6\)
In order to “calibrate” our data, an EBSD analysis of the grain was performed. The results are shown in the inverse pole diagram in Fig. 4. They prove that these grains are indeed of a different crystallographic orientation, one of them being basically of the (100) orientation.

Since theoretical data from other sources (5,11,12) are available for the DOS-induced reflectivity variations of low-index crystal faces of aluminum, we can compare the results for the grain number 2 (the lower one) with these. As the calculated data are often plotted with the energy scale referring to the Fermi level, in order to fit them to our energy scale referring to the vacuum level, we need to shift the x-axis by 4.28 eV, which is the value of the work function of aluminum.

Our data show a broad peak at about 8 eV (which has no support in DOS/R(E) calculations), a small narrow peak at about 12 eV and a possible very indistinct hump around 20 eV.

When comparing to Ref. 5) one finds that our sharp R(E) peak at around 12 eV above vacuum level is indeed predicted by the calculations (corresponding to the sharp drop in T(E) at around 16 eV above the Fermi level in Ref. 5)). As regards the broad peak between 15 and 20 eV above the vacuum level that is present in the theoretical DOS-induced reflectivity calculations of both Ref. 5) and Ref. 11), the comparison is not very conclusive. In our data there appears only a very indistinct hump. In Ref. 11) and Ref. 5), however, it is admitted that in this energy interval the theoretical calculations predict a negligible absorption although in reality this is not the case, due to incident beam coupling with the evanescent waves decaying slowly into the solid.

3.2 Single crystal aluminum samples

Single crystal aluminum samples with the orientation (100) and (111) were observed in the ultra-high-vacuum microscope. Series of micrographs were taken in the energy range of 0–20 eV and 0–90 eV. The measurements were done both on the argon-ion-sputtered site on the sample and on the native oxide covered part thereof. The signal from the sample (averaged over the field of view of a few \(m^2\)) was determined for each value of incident electron energy and the respective reflectivity-versus-energy curves were baseline subtracted to highlight peaks and valleys. The R(E) curves of the cleaned and the oxide-covered samples of Al(111) are shown in Fig. 5, those of Al(100) are shown in Fig. 6. They were then compared to theoretical predictions of very low energy reflectivity or transmissivity based on ab initio calculations,5,11,12,14 for an example see Fig. 7.

One can see that the difference between the R(E) of the clean surface and of the oxidized/contaminated one is quite marked. The R(E) curves of the argon-ion-uncleaned part of the aluminum (111) sample show an intensive broad hump at around 6.5 eV, while the clean part exhibits three peaks: at around 9 eV, a small one at 18 eV, a broader one at 24 eV, an indistinct one at approximately 36 eV and a large one at 44 eV. As follows from theoretical band structure calculations in Ref. 5), there should be peaks at \(E - E_{vac} = 9-10\) eV, between 11–13 eV, at approximately 18 eV, between 35–37 and 39–40 (that means at \(E - E_F = 13-14\) eV, between 14–17 eV, at 22 eV, between 39–41 eV and 43–44 eV). The calculated 11–13 eV peak is not visible in our data, and the 24 eV peak from our data is not mirrored in the...
calculations. Otherwise there is a qualitative agreement, even though our 44 eV peak is offset by a few eV: as Ref. 14) calculated from band structure, there should be a strong reflectivity peak due to the low density of states at around 41 eV above the vacuum level (45 eV with respect to the Fermi level).

The \( R(E) \) curves of uncleaned site on aluminum (100) have a peak at 4 and 14 eV, while the clean ones exhibit a peak at 6.5 eV, a shoulder at 12 eV, a broad peak between 26–30 and one at 49–50 eV with a shoulder at 63 eV. The peak at 6.5 eV has no support in the calculations, but as Ref. 5) notes, although \( k \) projected gaps in band structure are reflected as minima in \( T(E) \) maxima in \( R(E) \), some of these extrema may have also a more complicated origin. The \( R(E) \) shoulder at \( E - E_{\text{vac}} = 12 \) eV has a counterpart in the \( T(E) \) drop at \( E - E_F = 16 \) eV. Again, contrary to the theoretical calculations for Al(100) in Ref. 11), there are no visible \( R(E) \) features in the region of 15–20 eV. This was again attributed to absorption which was unaccounted for by the theoretical model in Ref. 11). The broad peak between 26–30 eV is in accordance with the band structure calculation in Ref. 11) (peak in \( R(E) \) at around \( E - E_{\text{vac}} = 28 \) eV) and Ref. 5) (the drop in \( T(E) \) that has a sharp minimum at \( E - E_F = 34 \) eV). The peak at \( E - E_{\text{vac}} = 49–50 \) eV should, according to Ref. 11) theoretical calculations, be positioned around 44 eV but others\(^ {15} \) reported its position to be at around 47 eV. According to Ref. 11) the used theoretical formalism for the calculation of band structure and theoretical \( R(E) \) and
T(E) performs inaccurately at higher energies. As Ref. 12 notes, inelastic effects cannot be reliably calculated and have to be inferred from a photoemission experiment.

4. Conclusion

The main advantage of the proposed method lies in its very high signal to noise ratio. This is achieved by the signal electrons being drawn together in the cathode lens field to a bundle, the major part of which impinges on the detector. When e.g. used to discern between differently oriented grains in a polycrystalline material, grain maps can be obtained in seconds this way, contrary to the Electron Back Scatter Diffraction (EBSD) method which takes minutes or longer. There appears to be a marked agreement between our experimental results and the theoretically calculated from the bandstructure (even though these calculations are not absolute and would require supporting data from photo-emission). As remarked by other authors,3,16 the influence of surface adsorbates and thin films on R(E) is dramatic in the very-low-energy region. This makes the method very surface sensitive, which on the other hand is rather a complication, since even in ultra high vacuum conditions it is difficult to make aluminum surface stay pristinely clean. This method offers the possibility of being a quick imaging technique that allows highlighting differences in the density of states of the whole observed area of the sample.

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REFERENCES