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Local Work Function Differences at Line Defects in Aluminium Oxide on NiAl(110)

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In recent years, atomic force microscopy has developed into an important tool to study surfaces with atomic resolution and is therefore applied in many different fields of science, for instance to understand surface chemistry on oxide surfaces. Apart from the topography of the surface atoms,[1–3] further details about the surface can be determined. In the Kelvin probe force microscopy mode, the contact potential difference, that is, the difference between the work functions of the sample and of the tip of the microscope, can be locally measured.[4–8] The work function is the minimum energy needed to remove an electron from the surface to a point outside of the surface.[9] This is especially relevant for reactions on surfaces with electron transfer, like redox reactions. Recently, the differences of the work functions have been determined with atomic resolution on differently charged adatoms[10] and in electrically charged defects.[11] The possible catalytic activity of these sites may be related to the shift of the work functions. However, it has to be noted that these irregularities have been electrically charged, and differences of the work functions are therefore not unexpected. In this communication we want to report on the application of Kelvin probe force microscopy to a thin film without artificially produced defects, here aluminium oxide on NiAl(110).

The experimental setup is a dual-mode low temperature (5 K) frequency modulation atomic force microscope (FM–AFM) and scanning tunnelling microscope (STM). FM–AFM detects the tip–sample interaction as a shift of the resonance frequency of the oscillating tip. A detailed description of the experimental setup can be found in refs. [12, 13]. The used sensor allows for simultaneous STM and AFM data acquisition. The feedback can be switched instantly between the STM and AFM mode. This means AFM and STM pictures of exactly the same position on the surface can be recorded with the same microscopic tip configuration, which shows the great advantage of this dual-mode device. The low temperature (5 K) during the experiments results in a very small thermal drift.[13,14] The metal tip is composed of 90% platinum and 10% iridium.

The studied system, thin film aluminium oxide on NiAl(110), is composed of two oxygen and aluminium layers.[15] The preparation is explained in detail in ref. [16]. The film grows in two reflection domains, A and B, which are tilted by $\pm 24^\circ$ with respect to NiAl[1 -1 0].[3] The structural defects on the film are reflection domain boundaries (A–B) and antiphase domain boundaries (A–A or B–B, abbreviated APDB). While the reflection domain boundaries occur randomly and rarely, APDBs occur regularly every roughly 8–10 nm. The APDBs release stress in the perfect oxide film which accumulates due to a small lattice mismatch between the oxide film and the NiAl along the [1 -1 0] direction. An AFM picture with atomic resolution of the 0.5 nm thin film is shown in Figure 1. The oxygen atoms in the complex surface unit cell of the domain and the APDB are clearly resolved. The APDBs are oxygen deficient with many unoccupied states in the aluminium band gap.[17] Therefore, they seem to be higher when pictured by STM (Figure 2). A higher chemical activity at the APDBs was shown by molecular beam methods.[18] More details on the structure of the film can be found in refs. [3, 15–17, 19, 20].

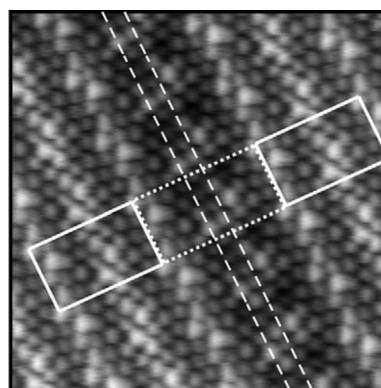

Figure 1. Atomic resolution AFM picture of thin film aluminium oxide on NiAl(110), 6 nm $\times$ 6 nm. The domains (B domain) and a straight APDB, which is pictured as dark depression, are visible. The white boxes indicate the unit cells on the domain. The dotted box indicates the unit cell at the APDB which is extended by 0.3 nm (dashed lines). The contact potential difference is balanced by a bias voltage of -0.22 V and the tip height was regulated to a frequency shift of -2.75 Hz.[3]

The contact potential difference between the tip and the sample is determined by AFM in the Kelvin probe force microscopy mode.[21] The tip and the sample are not in direct contact with each other but they are connected via the electronics. Their Fermi levels therefore align, leading to an electric field between tip and sample. The resulting additional (electrostatic) force shifts the resonance frequency of the tip to lower values.

A constant bias voltage applied between tip and sample superimposes the electric field. The recorded frequency shift vs bias voltage curves exhibit a parabolic dependence and the contact potential corresponds to the bias voltage at the maximum of the frequency shift (Figure 3 b).[21] The contact poten-

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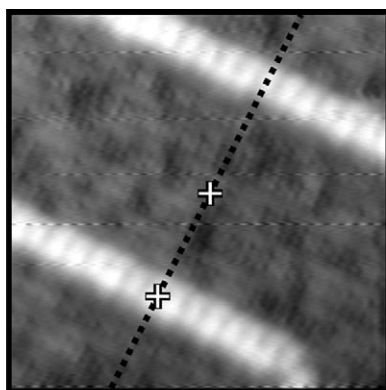

Figure 2. STM picture of thin film aluminium oxide on NiAl(110), 18 nm×18 nm. Two straight APDBs (bright) separating three A domains (dark) are visible. The dotted line represents the positions where the contact potential spectroscopy (Figure 4) was performed, the crosses indicate the positions of the spectroscopy in Figure 3. The bias voltage was +3 V and the tip height was regulated to a tunnel current of 100 pA.

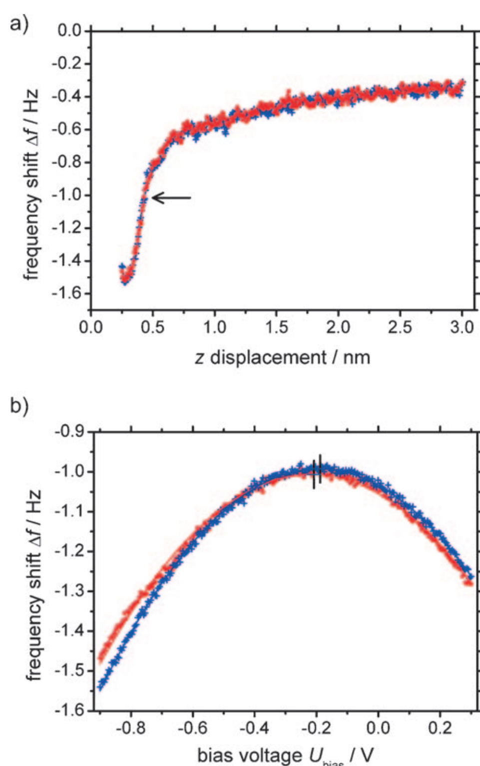

Figure 3. Force–distance and contact potential spectroscopy on thin film aluminium oxide on NiAl(110). a) The frequency shift as a function of the tip-sample distance, and therewith the force-distance curves, at the domain (blue crosses) and at the APDB (red bullets) are similar. The bias voltage was set to −150 mV to suppress electrostatic effects. The zero value of the *z* displacement is arbitrarily chosen. b) The contact potential is determined at the maximum of the frequency shift vs bias voltage curve. The contact potential at the APDB (red bullets) is smaller than at the domain (blue crosses). The tip height was constant during the measurement and corresponds to a frequency shift of −1 Hz at −150 mV (see arrow in Figure 3 a). The positions on the film are marked in Figure 2.

tial is determined by fitting the recorded frequency shift vs bias voltage curves with an quadratic term. The contact potential difference changes with different tip atoms and different tip geometries. Therefore, the measurements have to be performed with the same microscopic tip configuration.

The frequency shift vs distance curves are similar for the domain and the APDB (Figure 3 a). This means, in the range of measuring accuracy, the forces and the potential energies between tip and sample are the same.[22]

In Figure 4, the contact potential difference is plotted for positions along the line shown in Figure 2. The recorded contact potential at the APDB is roughly 20 meV smaller than at the regular domain, which was verified at many different sites. So, the work function at the APDB is smaller than at the domain.

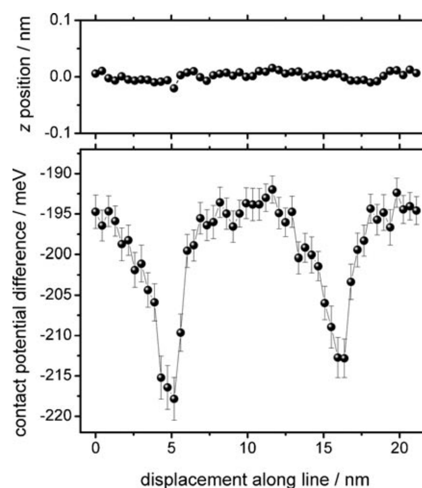

Figure 4. Contact potential difference on thin film aluminium oxide. The contact potential, which was determined at the positions at the line shown in Figure 2, decreases at the APDBs by approximately 20 meV. The tip height was constant during the measurement and corresponds to a frequency shift of −1 Hz at −150 mV. The contact potentials were determined by fitting the frequency shift vs bias voltage curves with a quadratic term (see Figure 3 b). The error bars represent the accuracies by which the maxima were determined. The upper plot shows the variation of the *z* position along the line in Figure 2, which is smaller than <0.03 nm.

It may be supposed that the real variation of contact potential difference is even larger, since the measured signal is the real contact potential difference convoluted with the tip geometry.[7,23] The influence of the APDB on the contact potential has approximately a full width at half minimum of 3 nm (see Figure 4). The lateral extension of the APDB was determined to 1.5 nm and the unit cell is expanded there by an additional row of oxygen atoms by 0.3 nm.[3] Assuming that the change of the contact potential is approximately located in this range (between 0.3 and 1.5 nm), the recorded contact potential is broadened by a factor of 2 to 10 due to the convolution with the tip. This means on the other hand, the contact potential difference is actually 2 to 10 times larger than recorded. Furthermore, it may be concluded that the tip is influenced by these defects over a distance of approximately 2–3 nm, which might be a reasonable estimation of the tip size. This gives also the lateral resolution of the measurements.

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The determined contact potential difference depends also on the tip–sample distance.[21] In general, a smaller distance increases the size of the interaction and the determined difference of the contact potential. If the distance is, however, too small, the probability that the tip restructures increases. Therefore, the tip–sample distance was set to a moderate value which corresponds roughly 50%–75% of the size of the maximum frequency shift (see arrow in Figure 3a).

The thin film aluminium oxide reduces the work function by approximately 0.5 eV from 4.8 eV for a pure NiAl(110) surface to 4.3 eV for the aluminium oxide film.[24] A further reduction of the work function at the APDBs may explain the higher reactivity at these linear defects. In ref. [18], it was shown that nitric oxide decomposition on thin film aluminium oxide happens preferentially at the APDBs, which may be explained by the smaller work function.

The stoichiometry of the film with an APDB was determined by DFT calculations to be $(NiAl)^{2-}_{substrate}(Al_{19}O_{28}Al_{28}O_{32})^{2+}$.[17] There, it was stated that unoccupied defect states in the film exist, which can be referred to as F^{2+} centre in the APDB. In our AFM measurements, we have recorded a shift of the local work function of approximately −20 meV at the APDB. This is in great agreement with the shift of −20 to −40 meV recorded at F^{2+} centres on MgO/Al(001)[11]. As it has been noted in earlier publications[21], the tiny difference between the two values is caused by the fact that the recorded contact potential difference depends on the tip–sample distance. The recorded change of the work function is in agreement with the DFT calculations where a shift of the valence and the conduction band with a local band bending at the APDB were predicted.[17] So, F^{2+}-like centres in the APDB, which have been predicted by DFT calculations, are now experimentally verified by FM–AFM.

By means of Kelvin probe measurements with a dual-mode FM–AFM/STM the local variation of the contact potential on thin film aluminium oxide on NiAl(110) was investigated. A significant work function decrease at the APDB was determined and F^{2+}-like centres, which have been theoretically predicted, were verified. The smaller work function at the defect sites is believed to be related to the higher chemical activity at these linear dislocations. So, AFM has shown to be an important tool for investigating surfaces and helps to understand surface chemistry. With this technique, the local variation of the work function may also be recorded at different systems, for instance at different sites at one single molecule.[25]

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