**Oxygen vibrations and acoustic surface plasmon on Be(0001)**

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Spectroscopic signatures of vibrational excitations on initially oxidized Be(0001) are identified by a combination of electron energy loss spectroscopy and density functional calculations. Prominent spectral features are due to vibrations in a Be-O mixing layer. Scanning tunneling microscopy indicates that initial oxidation occurs locally in the form of islands. The acoustic surface plasmon is still present on the oxygen-covered surface. Its dispersion has been determined along the ΓK direction and is virtually identical to the dispersion of the acoustic surface plasmon of the clean surface.

**I. INTRODUCTION**

The interaction of oxygen with metal surfaces is a topic of scientific and technological interest. Indeed, the oxidation of metals is a universal reaction since the oxide of most metals is more stable than the metal itself. The case of beryllium is particularly interesting since its surface can be easily oxidized even at low temperatures and in ultrahigh vacuum. Among many other technologically relevant properties, e.g., high melting point and low weight, its easy oxidation has made beryllium a preferred getter material for oxygen and water in nuclear fusion reactors. Owing to the general interest in fundamental processes occurring during metal oxidation and to the specific properties of beryllium it is not surprising that O₂ adsorption to Be surfaces has been investigated to some extent. A few experimental studies based on photoelectron and Auger electron spectroscopy reveal that surface oxidation begins at oxidation nucleation centers with subsequent lateral growth. Oxidation of Be can likewise occur via the dissociative adsorption of H₂O in a wide temperature range. In particular, at room temperature the H₂O molecule dissociates completely and oxidizes the surface by oxide island nucleation and growth. Less theoretical work on Be oxidation is available. These works consistently report that oxidation proceeds via the dissociative adsorption of O₂ molecules. Based on adsorption energy calculations a possible incorporation of O atoms into the Be(0001) surface has been suggested.

The (0001) surface of Be has further attracted considerable attention from both experimentalists and theorists owing to the existence of a two-dimensional plasmon with soundlike dispersion, which is referred to as an acoustic surface plasmon. In general, this kind of collective electron excitations exhibits low energies and is thus likely to participate in electron-phonon coupling phenomena such as superconductivity and in electron-photon interactions, which are the basis of plasmonics. The prerequisite for the occurrence of an acoustic surface plasmon is the coexistence of a partially occupied surface state band and the continuum of bulk electrons. Indeed, acoustic surface plasmons have been predicted for the (111) noble metal surfaces, which host a Shockley-type surface state and for Ag thin films. So far, they have been observed experimentally on Au(111) and Cu(111). Experimental evidence for surface acoustic plasmons have also been reported for metallic nanoparticles and for epitaxial graphene on Pt(111). Since electronic surface states are significantly affected by even small amounts of adsorbates, a question arises as to the influence of adsorbates on acoustic surface plasmons. It has been demonstrated in Ref. 16 that increasing exposure of Be(0001) to O₂ leads to a shift of the surface plasmon energy and a decrease of its intensity in vibration spectra. However, a clear-cut identification of oxygen vibration modes in the initial stage of oxidation of Be(0001) has not been reported so far. Moreover, the influence of adsorbates on the acoustic surface plasmon dispersion has been investigated scarcely. At present alkali metal adsorption on Be(0001) has been shown to distort the dispersion due to induced quantum well states.

In this article, vibrational spectroscopy with inelastically scattered electrons is combined with density functional calculations to suggest the structure of initially oxidized Be(0001) in ultrahigh vacuum. Emerging features in specular loss spectra are identified as signatures of vibrational excitations in a Be-O mixing layer. At the initial stage of oxidation the mixing layer occurs as separated Be-O islands as suggested by scanning tunneling microscopy (STM) images recorded at room temperature. Moreover, the dispersion of the acoustic surface plasmon has been determined along the ΓK direction of the Be(0001) surface Brillouin zone. Comparison with calculated dispersion data for clean Be(0001) (Ref. 16) reveals that the dispersion is virtually not affected by the initial oxidation.
II. EXPERIMENTAL AND THEORETICAL METHODS

Experiments were performed with an Ibach-type spectrometer in ultrahigh vacuum with a base pressure of $10^{-8}$ Pa and at room temperature. The incident monochromatic electron beam encloses an angle of $\vartheta = 65^\circ$ with the surface normal. The energy resolution of the spectrometer was set to 3 - 7 meV depending on the intensity of the vibrational signals. Dispersion data were acquired by angle-resolved measurements with a wave vector resolution of 0.01 Å$^{-1}$. To this end the analyzer of the spectrometer was rotated out of the specular scattering direction. The Be(0001) surface was cleaned by repeated cycles of Ar$^+$ bombardment and annealing. The progressive reduction of the oxide film thickness was monitored by X-ray photoelectron spectroscopy. Crystalline order was checked by low-energy electron diffraction. The Be(0001) surface was cleaned by conducting H$_2$ gas through a heated capillary.

Total energy calculations were performed within the framework of density functional theory (DFT) employing ultrasoft pseudopotentials and the Perdew-Burke-Ernzerhof general gradient approximation for the exchange and correlation energy functional. The dynamical properties at the $\Gamma$ point were calculated by applying density functional perturbation theory (DFPT) included in the QUANTUM-ESPRESSO package. The electron wave functions were expanded in plane waves with an energy cutoff of 32 Ry (1 Ry = 13.6 eV) while for the effective potential and the charge density an energy cutoff of 288 Ry was used. The integration over the surface Brillouin zone was carried out over a $(8 \times 8 \times 1)$ Monkhorst-Pack division of the k-points, and a finite temperature smearing of the Marzari-Vanderbilt type set to 0.03 Ry. The atomic arrangement was obtained by minimizing the total energy with respect to the positions of the atoms. The working slab includes 14 ($\sqrt{3} \times \sqrt{3}$)-Be(0001) layers (3 Be atoms in each layer) and 2 oxygen atoms on each side of the slab surface. Each repeating slab was separated by 18 Å of vacuum perpendicular to the surface. The structure was optimized without any constraints on symmetry until the resulting forces acting on individual atoms were less than 25 meV Å$^{-1}$.

III. RESULTS AND DISCUSSION

A. Oxygen vibrations

Figure 1 shows the time evolution of vibrational spectra acquired from Be(0001) in specular scattering geometry. A sharp feature at 20 meV and rather weak and broad signatures at 42 and 106 meV have been observed 1 h after the last cleaning cycle (bottom line in Fig. 1). Calculations (see below) reveal that peaks at 20 and 42 meV are due to Be vibrations while spectral weight at 106 meV originates from vibrations in a Be-O mixing layer. While the peaks at 20 and 42 meV do not vary strongly within 60 h the spectra at higher vibration energies exhibit considerable changes. Starting from 10 h in ultrahigh vacuum spectra from Be(0001) surfaces exhibit a loss peak at 72 meV, which with increasing time exhibits an increasing vibrational energy. After 50 h a further energy increase fell below the detection limit. Similar energy shifts have been reported for dipole-active perpendicular Li vibration modes on various metal surfaces in the low-coverage range. This energy increase has been interpreted in terms of dipole-dipole interactions between the adsorbed alkali metal atoms. An additional broad contribution appears at 132 meV starting from 10 h after the last cleaning cycle and likewise increases in intensity. The initially observed spectral feature at 106 meV is hardly discernible since it is flanked by the increasingly strong peak at 77 meV and the rather broad feature at 132 meV. For energies exceeding 150 meV the specular loss spectra remain virtually featureless. A faint feature around 180 meV becomes discernible after 60 h and may be due to the presence of atomic hydrogen. Off-specular loss spectra acquired from Be(0001) that stayed in ultrahigh vacuum for more than 10 h exhibit additional features in an energy range of 150 to 450 meV. These loss features are most likely the spectroscopic signatures of H and OH vibration modes (see below). As a first result, cleanliness of Be(0001) degrades on a time.
FIG. 2. (Color online) Comparison of specular spectra acquired from clean Be(0001) after exposure to the residual gas of the ultrahigh vacuum for 60 h (black) and after exposure to 10 L \( \text{O}_2 \) (red). Impact energy: 8 eV, count rate of elastic peak: \( 120 \times 10^3 \text{ s}^{-1} \), FWHM of elastic peak: 4 meV.

To identify the origin of the spectroscopic signatures presented in Fig. 1 clean Be(0001) was exposed to \( \text{O}_2 \). The reason for choosing \( \text{O}_2 \) is the easy oxidation of Be, which in ultrahigh vacuum occurs via dissociative adsorption of residual \( \text{H}_2\text{O} \). The top vibational spectrum presented in Fig. 2 is a specular spectrum acquired from Be(0001) after exposure to 10 L \( (1 \text{ L} = 10^{-4}\text{ Pa.s}) \) \( \text{O}_2 \), while the bottom spectrum results from a cleaned surface that stayed 60 h in ultrahigh vacuum. Both spectra look similar. Indeed, the most prominent feature in both spectra is a loss peak at 77 meV. Likewise the broad peaks at 106 and 132 meV and the rather sharp decrease of vibrational signal at 150 meV is observed from both spectra. The top spectrum exhibits a slightly higher intensity of the peak at 77 meV which possibly results from a higher oxygen coverage. This interpretation is in line with the higher intensity of the high-energy wing of the peak at 77 meV and that peaks at 20 and 42 meV are hardly discernible. The clean sample has likewise been exposed to \( \text{H}_2 \), which gives the dominant contribution to the mass spectrum of the residual gas in the vacuum recipient. However, even at elevated exposures exceeding 100 L specular vibration spectra are essentially identical with those of the clean surface, i.e., hydrogen in its molecular form does not adsorb on Be(0001) at room temperature. This result is in agreement with earlier findings. Exposing clean Be(0001) to atomic hydrogen does lead to adsorption but the resulting vibration spectra of the \( \text{H} \)-covered surface differ strongly from those of the \( \text{O}_2 \)-exposed sample. Consequently, based on the adsorption experiments contributions to vibration spectra at 77, 106 and 132 meV (Fig. 1) are likely due to oxygen-related vibrations. To unravel the origin of peaks at 20 and 42 meV and to clarify the adsorption structure calculations have been performed.

The proposed structure based on the DFT calculations is illustrated as top [Fig. 3(a)] and side [Fig. 3(b)] views. O and Be atoms appear with red and gray color, respectively. Inequivalent O atoms are denoted \( \text{O}_A \) and \( \text{O}_B \). The dashed line shows the boundaries of the unit cell in the \(xy\) plane that has been used in the calculations. The in-plane lattice parameter of this cell is 3.95 Å. The side view [Fig. 3(b)] shows that the topmost Be layer is sandwiched between a bilayer of oxygen, in which the top (bottom) layer is formed by \( \text{O}_A \) (\( \text{O}_B \)) atoms. Each oxygen layer \( \text{O}_A \), \( \text{O}_B \) exhibits a \( (\sqrt{3} \times \sqrt{3}) \)-R30° structure referring to the hexagonal structure of the sandwiched Be layer. The \( \text{O}_A \) and \( \text{O}_B \) lattices are shifted to each other, however not rotated (Fig. 3). The separation of \( \text{O}_A \) and \( \text{O}_B \) atoms in the surface normal direction \( z \) is 1.11 Å. The topmost layer \( \text{O}_A \) resides 0.66 Å above the Be layer while the bottom oxygen layer \( \text{O}_B \) is located 0.45 Å below. In the following, this layer containing Be, \( \text{O}_A \), and \( \text{O}_B \) atoms is referred to as the Be-O mixing layer. The distance between the Be-O mixing layer and the second Be layer is 1.67 Å. Several structures were tested. However, based on (i), the calculated binding energy of the adsorbed oxygen atoms, (ii), the dynamic stability of the structure and, (iii) the fairly good agreement between the calculated and measured phonon spectrum with respect to the energy and relative intensities of four distinct modes to be discussed below, we propose the atomic structure displayed in Fig. 3.

The phonon structure is obtained from the DFPT calculations. To ensure the good quality and reliability of the calculations the phonon dispersion relations of clean Be(0001) were calculated. Figure 4 shows a comparison of our calculations with previously reported data. Especially the calculated energy of the Rayleigh wave (circles) at the M point of the surface Brillouin zone is well reproduced, which is an improvement to a previ-
FIG. 4. Calculated phonon dispersion curves of clean Be(0001) along the indicated directions of the surface Brillouin zone. The distance between Γ and M (K) is 1.59 Å⁻¹ (1.84 Å⁻¹). Experimental data appear as circles (Rayleigh wave) and dots and have been adopted from Ref. 42.

ous report.⁴² The dispersion curves reveal that at Γ a variety of Be modes in an energy range of 6 to 83 meV are present. Calculated Be vibration modes at 17 and 40 meV may correspond to the experimentally observed loss peaks at 20 and 42 meV in specular spectra (bottom spectrum in Fig. 1). The absence of the other calculated modes from specular spectra may be due to their weak dynamical dipoles or low excitation cross section. The excitation cross sections varies with the primary energy of impinging electrons. Indeed, using a primary energy of 7 eV leads to loss peaks at 12 and 20 meV (not shown) rather than at 20 and 42 meV in spectra acquired at 8 eV (Fig. 1).

When atomic oxygen is adsorbed the calculations reveal several vibration modes that are mainly localized in the Be-O mixing layer. The calculated phonon density of states (DOS) at Γ is plotted along with experimental data acquired in specular scattering geometry from Be(0001) exposed to 10 L of oxygen in Fig. 5. Additionally, the O-covered surface had been annealed at 600 K for several minutes. The annealed surface most likely exhibits a structure that resembles the relaxed structure of the calculations more closely than the surface solely exposed to O₂. Together with the total phonon DOS of the Be-O mixing layer (shaded area) contributions from vertical atom displacements are displayed as a full line. The energies of the dominant loss peaks in experimental spectra, i.e., 80, 109, 125, and 138 meV, are closely reproduced by the calculations. The phonon DOS peaks at 75, 112, 130, and 136 meV. The calculated peak at 75 meV exhibits most contributions from shear-vertical displacements while the three higher energy modes show dominant contributions from displacements in the surface plane. In addition to the accordance between calculated and measured vibration energies the calculated relative intensities of the above-mentioned modes are in qualita-

tive agreement with the experiment.

Figure 6 illustrates the atom displacements, i.e., the predominantly shear-vertical phonon at 75 meV [Fig. 6(a)] and the vertical displacement patterns at 112 meV [Fig. 6(b)] and at 130 meV [Fig. 6(c)]. The phonon mode at 75 meV clearly shows large shear-vertical displacements of the O₈ atoms together with the Be atom below while the other atoms have much smaller vertical displacements. The smaller vertical atom displacements for the phonon modes at higher energy may be responsible for a smaller dynamic dipole moment, which may ex-
plain the experimentally observed low count rate of these modes in specular vibration spectra. The displacement pattern of atoms in the 112 meV mode is very similar to that of the 75 meV mode. However, the in-plane displacements of Be atoms of the topmost layer are much more pronounced than observed from the 75 meV mode. The mode at 130 meV [Fig. 6(c)] likewise gives a rise to a spectroscopic signature in vibration spectra. The characteristics of this mode are the O$_{\text{A}}$ atoms having a larger vertical displacements than the O$_{\text{B}}$ atoms. Further, the surrounding Be atoms exhibit considerable in-plane motions.

Before discussing the dispersion of the acoustic surface plasmon we comment on two observations. The experimentally observed peak at 80 meV (Fig. 5) has slightly shifted from 77 meV measured from samples prior to annealing (Fig. 2). This shift may be caused by structural changes of the oxygen layer induced by annealing.

Further, low-energy electron diffraction patterns do not show any hint to the (111) reflections of the oxygen layer induced by annealing. Even elevated O$_2$ exposures of 100 L result in diffraction patterns that are virtually identical to the diffraction pattern of clean Be(0001) (inset to Fig. 1). In particular, no additional diffraction spots appeared, which would be expected for a superstructure with long-range periodicity. This observation is in agreement with an earlier investigation into low-energy electron diffraction patterns of initially oxidized Be(0001). It has been shown in Ref. 5 that room-temperature deposition of oxygen does not lead to additional diffraction patterns up to 120 L. Only annealing samples exposed to $\approx$ 100 L at $\approx$ 700 K results in additional diffraction beams. These findings were interpreted in terms of bulk-like BeO nuclei at submonolayer oxygen coverages by which initial oxidation of the surface proceeds. Further experimental evidence for the BeO nuclei is provided by STM images. Figure 6 shows a typical STM image of Be(0001) exposed to 10 L of O$_2$. Two adjacent substrate terraces are visible, on which irregularly shaped protrusions are distributed. We assign these structures to local areas of the Be–O mixing layer for several reasons. Similar structures were reported from metal surfaces exposed to O$_2$ at room temperature, i.e., Pt(111), Cr(110), Mg(0001), and Pt(110). Further, increasing the exposure of Be(0001) to O$_2$ leads to an increased amount of islands that partly coalesce and thus increase the coverage of the observed structures. In addition, the protrusions appear with an average apparent height of 1 Å. The calculated distance between the topmost O layer and the first Be layer is 0.66 Å. Experimentally it was difficult to achieve stable imaging conditions in particular at negative voltages. Between 0.4 and 1.6 V, however, the apparent height of the islands did not vary considerably. Obviously, the Be–O islands do not form a closed film and no long-range ordered patterns are visible, which is probably the origin of the missing diffraction pattern of the superstructure.

To our knowledge Fig. 7 shows the first wide-range STM image of Be(0001). So far, small areas have been imaged to analyze Friedel oscillations of a Be(0001) electronic surface state. The wide-range STM images acquired during the present work reveal that the vast majority (90 %) of apparent step heights is (3.2 ± 0.3) Å, which agrees reasonably well with the lattice parameter along the (0001) direction (3.6 Å). Step heights of 1.8 Å, i.e., half the lattice parameter along the surface normal, were less abundant. While a quantitative analysis of the distribution of step heights is beyond the scope of this work, we note that for the (0001) surface of alumina it has been shown that the statistical distribution of step heights depends on the details of sample preparation.

B. Acoustic surface plasmon

While the acoustic surface plasmon dispersion has been calculated for the $\Gamma M$ and the $\Gamma K$ directions of the Be(0001) surface Brillouin zone, it has been experimentally reported for the $\Gamma M$ direction only. It was argued that along $\Gamma K$ interband transitions involving a Be(0001) surface state at M have a more detrimental effect on the acoustic surface plasmon than along $\Gamma M$. Spectroscopic signatures of the acoustic surface plasmon along $\Gamma K$ turned out to be rather weak and broad, which may be partly caused by the reason mentioned above and partly by the presence of adsorbates. A typical spectrum is shown in Fig. 8(a) for a momentum transfer of $q_{\perp} = 0.26 \text{ Å}^{-1}$ along $\Gamma K$. The broad feature centered at 1.33 eV is interpreted as the signature of the acoustic surface plasmon. This assignment is corroborated by the agreement between experimental and calculated dispersion data depicted in Fig. 8(b). To acquire angle-resolved vibration spectra the impact energy of electrons has been fixed to 8 eV and the analyzer has been rotated out of the specular scattering direction ($\theta = 65^\circ$) by an angle $\varphi$. 

FIG. 7. (Color online) Constant-current STM image acquired at room temperature from a cleaned Be(0001) surface exposed to 10 L of O$_2$ (0.5 V, 1 nA). The color scale ranges from apparent heights between 0 and 8.5 Å. Islands with irregular circumference and an average apparent height of 1 Å are assigned to local areas of the Be–O mixing layer. The arrow indicates impurities.
FIG. 8. (Color online) (a) Electron energy loss spectrum acquired in off-specular scattering conditions with a momentum transfer of $q_\parallel = 0.26 \text{Å}^{-1}$ along $\bar{\Gamma}K$. The broad feature centered at 1.33 eV is due to the acoustic surface plasmon. Additional peaks between 0.15 and 0.45 eV originate from H and OH vibrations (see text). (b) Energy of the acoustic surface plasmon as a function of parallel momentum transfer along $\bar{\Gamma}K$. Experimental data appear as circles. Calculated data have been adapted from Ref. 51 and are depicted as dots. The dashed line indicates an extrapolation of the linear dispersion from low to high parallel wave vectors. The slope is $\approx 6.4 \text{ eVÅ}^{-1}$ (Ref. 15).

ranging from $0^\circ$ to $12^\circ$. The parallel momentum transfer of an electron scattered from a vibrational excitation with energy $h\omega$ and detected at an angle $\vartheta - \varphi$ with respect to the surface normal is calculated as

$$q_\parallel = \frac{\sqrt{2mE_0}}{h} \left[ \sin \vartheta - \sqrt{1 - \frac{h\omega}{E_0} \sin(\vartheta - \varphi)} \right],$$

where $E_0$ denotes the energy of the incident electrons, $m$ is the free electron mass, and $h$ the Planck constant divided by $2\pi$. Based on the agreement between experimental and calculated data [Fig. 8(b)] the influence of the initial oxidation of Be(0001) on the dispersion of the acoustic surface plasmon is negligible. In particular, the slope of the dispersion curve for small parallel wave vectors appears to be virtually identical. The dashed line in Fig. 8(b) depicts an extrapolation of the linear dispersion expected for small wave vectors to higher values of $q_\parallel$. The slope of this dispersion curve is given by the Fermi velocity of the Be(0001) surface state.15 Possible explanations for the observed persistence of the surface acoustic plasmon are the following. Our calculations of the Be(0001) electronic structure indicate that the surface state of pristine Be(0001) at $\bar{\Gamma}$ shifts to lower energies upon increasing O coverage. At full coverage this surface state is completely filled, mainly by electron donation from O$_\text{p}$ atoms. The data presented here were acquired from a Be(0001) surface which had been partly covered with oxygen. Therefore, the surface state at $\bar{\Gamma}$ is not completely occupied and sustains the surface plasmon. Moreover, according to the calculations the surface state at M is not affected by the presence of oxygen and thus may support the occurrence of the acoustic surface plasmon. In contrast to the present findings, K adsorption on Be(0001) does lead to a modification of the slope of the dispersion curve, which has been attributed to K-induced quantum well states.29

Due to the low intensity of the plasmon losses long data acquisition times were necessary for an acceptable signal-to-noise ratio. The inevitable contamination of the Be(0001) surface leads to further loss features at 156, 185, 360 and 413 meV [Fig. 8(a)]. These signatures appeared with significant intensity in off-specular loss spectra whilst in specular spectra they were hardly discriminated from the background. The comparison with previously reported results reveals that peaks at 156 and 185 meV may be assigned to vibration modes of atomic hydrogen.39 The loss energies of 360 and 413 meV may be related to vibration modes of hydroxyl groups.45,52 The presence of atomic hydrogen and hydroxyl groups on the initially oxidized Be(0001) surface is likely due to the dissociation of residual H$_2$O.6,53 In Ref. 6 it has been shown that H dissociated from H$_2$O is trapped in the oxide layer.

IV. SUMMARY AND CONCLUSIONS

Inelastic electron scattering and density functional calculations unravel the geometric structure of Be(0001) in its initially oxidized state. The formed Be-O mixing layer reflects the strong reorganization of the light an reactive beryllium atoms when oxygen is adsorbed. The proposed atomic structure is supported by a fair agreement between experimental and calculated spectroscopic signatures of four distinct Be-O vibrational modes with respect to their energies and relative intensities. While the two topmost Be layers are considerably modified due to the presence of O atoms, the dispersion of the acoustic surface plasmon is not significantly affected by the Be-O mixing layer.

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