Work function reduction by BaO: growth of crystalline barium oxide on Ag(001) and Ag(111) surfaces

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Abstract

Ultrathin films of barium oxide were grown on Ag(001) and Ag(111) using the evaporation of Ba metal in an O₂ atmosphere by molecular beam epitaxy. Ultraviolet photoemission spectroscopy reveals that films consisting of predominantly BaO or BaO₂ result in Ag(001) work function reductions of 1.74 eV and 0.64 eV, respectively. On the Ag(001) surface, Ba oxide growth is initiated by two-dimensional nucleation of epitaxial BaO, followed by a transition to three-dimensional dual-phase nucleation of epitaxial BaO and BaO₂. Three-dimensional islands of primarily BaO₂(111) nucleate epitaxially on the Ag(111) substrate leaving large patches of Ag uncovered. We find no indication of chemical reaction or charge transfer between the films and the Ag substrates. These data suggest that the origin of the observed work function reduction is largely due to a combination of BaO surface relaxation and an electrostatic compressive effect.

I. Introduction

The alkaline-earth oxides are important materials in a variety of technologies. Recent research has focused on their use in electronics [1], catalysts [2-6], and cathode technologies [7-12]. Of particular interest are recent reports that propose the epitaxial growth of alkaline earth oxide thin films on crystalline metal substrates to produce robust near-ultraviolet photocathodes. Other desirable photocathode properties, such as reduced work function, increased quantum efficiency, and low thermal emittance are predicted for such hybrid photocathode materials[13]. Thin epitaxial films of MgO on Ag(001) have been shown to lower the work function of Ag by approximately 1.3 eV relative to clean Ag(001)[14], as well as increase quantum efficiency and produce more directed photoemission[13], consistent with theoretical predictions [11]. While the MgO/Ag(001) system exhibits promising results for photocathode applications, theoretical predictions of work function reductions of up to 4.1 eV have been made for other alkaline oxides on metal supports [7, 8, 11]. These calculations consistently predict that thin epitaxial BaO films will produce the largest work function reduction of the various alkaline earth oxide/metal heterostructures.

The most widely studied material combination consists of BaO films on W supports. This system can be used as a low-temperature thermionic cathode material[15]. It has been shown that Ba metal adsorbed on the (100), (110), and (111) faces of W results in a lowering of the work function and an increase in thermionic emission[16]. However, these surfaces are highly susceptible to oxidation and despite a slight increase in the work function of the system upon initial oxidation, the formation of a BaO film results in a further lowering of the work function. Hong *et al.* [17] studied the initial oxidation of Ba/W(110) and concluded that oxygen first incorporates underneath the Ba overlayer, and then forms an oxide on top of the Ba adlayer. Despite these structural complexities, these authors found that exposure of the Ba/W(110) surface to oxygen results in a further lowering of the work function. However, gaining a detailed understanding of the relationship between structure, interface composition, and electronic properties is made difficult by the oxidation of the substrate and the formation of BaO_{1+x} . Oxidation (or passivation) of the substrate surface and the difficulties associated with preserving a crystalline interface have hindered efforts to grow epitaxial BaO. A few groups have shown that crystalline BaO can be grown on various substrates at temperatures as low as room

temperature using molecular beam epitaxy (MBE) [18-21], or laser-molecular beam epitaxy [22]. Yasir *et al.* [21] and Pindoria *et al.* [19] deposited Ba in an oxygen environment on GaAs(100) and SrTiO₃(001) substrates, respectively. The lattice mismatch between BaO and SrTiO₃(001) is reduced to 0.3% if the BaO rotates by 45° about [001]_{STO}. BaO might also grow epitaxially on Ag(001) with a 45° rotation about [001], although the in-plane lattice mismatch is -4.5%.

Here we take advantage of the relatively high oxidation resistance of Ag to explore the nucleation, growth and properties of crystalline barium oxide films on Ag(001) and Ag(111) by MBE. We find that the first monolayer (ML) consists of BaO on Ag(001) and that subsequent layers either propagate the rocksalt BaO structure, or oxidize to tetragonal BaO₂, depending upon the oxygen pressure. Epitaxial BaO₂ islands nucleate during the initial stages of growth on Ag(111) and remain the majority phase, although some BaO also forms. *In-situ* x-ray photoemission spectroscopy (XPS) reveals negligible charge transfer between BaO and Ag. Ultraviolet photoemission spectroscopy (UPS) reveals that the work function of Ag(001) is reduced for all BaO predominant films up to 8 ML in thickness, independent of the concentration of the BaO₂ sub-phase.

II. Experimental

Single crystals of Ag(001) and Ag(111) were initially cleaned by repeated cycles of Ar ion sputtering and ultra-high vacuum annealing at 500 °C prior to growth. Ba was evaporated from an effusion cell. Barium oxide (BaO_x) films were grown via MBE by depositing Ba in an O₂ ambient introduced into the deposition chamber through a mass flow controller. Neither activated oxygen nor ozone was used in order to avoid substrate oxidation. It has been shown previously that Ag does not oxidize in O₂, but is readily oxidized in either atomic oxygen or ozone[23]. The Ba flux was measured prior to film growth with a quartz crystal microbalance (QCM) in the O₂ ambient using the density and Z-factor of BaO. The Ba flux during deposition was 0.0045 ML/s. For most films, the oxygen flow rate and pressure during deposition of BaO were 0.1 sccm and 2×10^{-7} torr. In order to maximize the extent of oxidation to BaO₂ in select films, the oxygen rate was increased to 0.5 sccm (1.3×10^{-6} torr). The temperature was varied to optimize the epitaxial quality and surface morphology of 1 ML BaO on Ag(001). As reported elsewhere for SrTiO₃ substrates [19], epitaxial BaO was observed to nucleate for substrate temperatures ranging from 100 °C to 400 °C. A substrate temperature of 200 °C was used unless

otherwise noted. Substrate temperatures below 200 °C resulted in pronounced streak modulation in the reflection high-energy electron diffraction (RHEED) patterns, indicating film roughness, as well as some degree of polycrystalline texture.

Immediately following the post-sputter UHV anneal at 500 °C, the substrates were cooled to the growth temperature while the Ba effusion cell temperature was increased. During this time, the flow of oxygen was initiated while the effusion cell temperature was stabilized. The flux from the effusion cell was then re-measured and optimized immediately prior to film growth. The operational stability from effusion cells loaded with alkaline metals has been observed to vary with oxygen pressure [24]. As a result, the flux was measured under identical conditions to those used during film growth, assuming exclusive formation of BaO for the QCM parameters. After checking the Ba flux and allowing the temperature of the substrate to stabilize, the effusion cell shutter was closed, the sample was moved into the growth position, and the source shutter was re-opened. To end the growth, the sources shutter was closed, the flow of oxygen stopped, and the sample cooled to room temperature. Immediately following film growth, *in situ* UPS and XPS measurements were carried out in an appended chamber using VG/Scienta monochromatic He I α UV (21.2 eV) and monochromatic Al K α x-rays (1486 eV) for excitation, respectively, and an R3000 electron spectrometer for analysis.

III. Results and Discussion

Ba oxide nucleation and growth proceed quite differently on Ag(001) and Ag(111). Figure 1 shows the evolution of the RHEED patterns during the initial stages of Ba oxide growth on these two substrate orientations. The left side shows diffraction patterns for clean Ag(001) (a), as well as BaO monolayer-equivalents (ML-EQ) of 0.5 (b), 1.0 (c), and 2.0 (d). These data reveal a Stranski-Krastanov (SK) type growth mode with the wetting layer consisting of BaO. Interestingly, at least partial film relaxation occurs after the first 0.5 ML-EQ, as revealed by the appearance of a new pair of streaks characteristic of relaxed BaO (Fig. 1b). These streaks remain present and grow in intensity up to 2 ML-EQ, at which point second-order BaO streaks appear, along with a pair of streaks characteristic of relaxed BaO₂ (Fig. 1d). Intensity modulation within the BaO₂ streaks indicates 3D island growth, giving rise to a SK-type growth mode with epitaxial BaO₂ islands nucleating atop the BaO wetting layer.

Figure 1 e-h show an equivalent set of diffraction patterns for Ba oxide on Ag(111) under the same set of deposition conditions. In contrast to what happens on Ag(001), Ba oxide nucleates primarily as oriented islands of BaO_2 , with the corresponding streaks first appearing faintly at 0.5 ML-EQ and then growing stronger at 1 ML-EQ, with second-order streaks appearing at 2 ML-EQ. The RHEED streaks associated with the substrate weaken but do not disappear even up to 8 ML-EQ (not shown). Ba oxide thus initially nucleates primarily as BaO_2 islands (Volmer-Weber growth) which remain at higher thickness. Very weak streaks associated with $\text{BaO}(111)$ appear at 2 ML-EQ. The lattice mismatch

between $\text{BaO}_2(111)/\text{Ag}(111)$ is -7.5% along the $[110]$ direction while that for $\text{BaO}/\text{Ag}(111)$ is +1.4% using the coincidence site lattice model[25], where every 3 Ba atoms are nearly

Fig. 2.

FIG. 1.

coincident with every 4 Ag atoms. Thus, based upon lattice mismatch alone, BaO formation is favored. However, the (111) orientation of BaO is polar and, therefore, inherently unstable. Bowman *et al.* [18] attempted to stabilize the $\text{BaO}(111)/\text{Pt}(111)$ and found that a 2×2 surface reconstruction readily forms in order to eliminate the surface dipole. In our case, we see no evidence for the formation of BaO with or without a surface reconstruction by RHEED during the initial stages of growth. Instead, formation of non-polar BaO_2 is initially energetically favored.

Figure 2 displays line profiles for 0 and 2 ML-EQ taken from the RHEED patterns in Figure 1.

For the (001) orientation (Fig. 2a), streaks at ~ 55 pixels and ~ 110 pixels correspond to the lattice spacing for BaO(001), and there is no measurable intensity at the streak spacing for Ag(001) (~ 67 pixels), indicating complete surface coverage. In addition, the streaks just below ~ 100 pixels correspond to the streak spacing for BaO₂. In contrast, deposition on Ag(111) results in incomplete extinction of the peaks at pixels 75 and 150 which correspond to diffraction from exposed Ag(111). The diffraction peaks corresponding to the d spacing of BaO₂ are evident at pixels 60 and 120.

Figure 3 displays Ba $3d_{5/2}$, O $1s$, and Ag $3d$ core-level photoemission spectra taken at normal emission for ~ 4 ML-EQ Ba oxide on Ag(001). The Ba $3d_{5/2}$ peak is highly asymmetric and can be fit using two peaks, corresponding to BaO and BaO₂, with a binding energy (BE) difference of ~ 1.5 eV. We assign the higher BE of the two peaks to BaO₂ based on initial-state charge transfer considerations. Both chemical species exhibit an anomalous negative binding energy shift relative to Ba metal (BE = 780.5 eV). This negative BE shift was also observed in the initial oxidation of Ba on W(110) and was attributed to hybridization of Ba $5d$ orbitals with both W $5d$ and O $2p$ orbitals [26]. Alternatively, the increase in Ba $3d$ BE expected in going from Ba⁰ to Ba²⁺ for the free atom has been calculated to be overshadowed by the BE decrease resulting from the Madelung potential at the Ba site associated with the rocksalt BaO structure[27]. The BE increase expected on purely electrostatic grounds in going from Ba⁰ to Ba²⁺ is small because of the large size of the Ba atom.

Fig. 3.

A large chemical shift between BaO and BaO₂ is also present in the O 1s core-level spectra shown in Figure 3b. Peaks assigned to BaO and BaO₂ fall at 527.5 eV and 530.6 eV respectively. This assignment is reasonable since BaO₂ has a peroxide structure for which the formal charge on each O anion is -1. Based on their initial-state charge distributions, peroxides should exhibit a higher O 1s binding energy than oxides which have a formal charge of O²⁻. This result agrees quite well with the chemical shift observed during the oxidation of Ba on the θ -Al₂O₃/NiAl(100) surface [3]. These authors assigned the two O 1s peaks to BaO and BaO₂²⁻ (barium peroxide), and observed a chemical shift of 2.9 eV between them. As a double-check of these assignments, we compared the peak area ratio of BaO:BaO₂ determined using the Ba 3d_{5/2} peak to the ratio using the O 1s peak areas assigned to the two phases. Within experimental uncertainty, the ratios using the two core-level peaks agreed with each other after accounting for the 1:2 ratio (BaO:BaO₂) expected when using the O 1s. In contrast, the Ag 3d_{5/2} peak at 368.2 eV and the Ag 3d_{3/2} peak at 374.1 eV can be fit to **symmetric** singlets associated with Ag metal (Fig. 3c). There is no evidence for the formation of any of the oxides of Ag during Ba oxide nucleation, as expected when using O₂ as the oxidant. This result **and the lack of asymmetry** also suggests that there is little electron transfer between the Ag and either oxide.

Analogous core-level spectra are shown for the Ag(111) orientation in Figure 4. The lower (upper) binding energy components for both the Ba 3d_{5/2} and O 1s core levels are again attributed to BaO (BaO₂), and both oxides exhibit a Ba 3d_{5/2} binding energy lower than that of Ba metal. In contrast to the results for deposition on Ag(001), however, peak area analysis reveals that the dominant species on Ag(111) is BaO₂, consistent

Fig. 4.

with the RHEED results. Indeed, only 25 - 40% of the film(s) typically consists of BaO. The measured chemical shifts are very similar to those for films on Ag(001), and the expected approximate 2-to-1 peak area ratio is again borne out. Interestingly, due to the Volmer-Weber growth mode, there is still enough intensity in the Ag 3*d* satellite features at ~372 eV and ~378 eV that fitting only the stronger spin-orbit split Ag 3*d* peaks at 368.2 eV and 374.1 eV is not possible. However, if the Ag 3*d*_{5/2} peak alone is included, a very good fit can be achieved with only one component, as seen in the inset to Figure 4c, similar to the Ag(001) case. This result is again suggestive of little or no electron transfer or chemical reaction between the Ag(111) and BaO₂.

Much of the interest in Ba oxide layers on metal supports is due to the sometimes dramatic work function reduction that can be realized relative to the clean metal. We have used UPS to determine the work function for two specimens: (i) predominantly BaO, and, (ii) predominantly BaO₂, both deposited on Ag(001). For clarity, the two specimens will be referred to as BaO and BaO₂, although a fraction of the minority phase is present in each sample. Examination of the RHEED patterns (not shown) during the growth optimization phase suggest that the initial interfacial wetting layer is composed of BaO. It

has been suggested that O₂ will adsorb and disassociate to form the stable peroxide at the surface[28]. Nucleation of predominantly BaO₂ was achieved using higher substrate temperatures and an oxygen flow and partial pressure five times larger than that used to achieve chiefly BaO. Figure 5a displays UPS spectra for both samples. Interestingly, most of the major features are seen in both spectra. One of the two marked changes between the BaO and BaO₂ samples is that the broad peak observed at ~3 eV in the BaO/Ag(001) sample is virtually absent in the BaO₂/Ag(001) sample. This loss of intensity suggests that the bandgap of BaO₂ is larger than that of BaO. The other noticeable difference between the two spectra is that the high binding energy edge occurs

at a much higher value for BaO/Ag(001) than for BaO₂/Ag(001), revealing a lower work function for the former. The difference between the incident photon energy and the high-binding energy cutoff defines the work function. Therefore, BaO/Ag(001) is found to have a lower work function than BaO₂/Ag(001). This result is in agreement with that of Haas *et al.*, [29] who found a clear anti-correlation between the oxygen binding energy and the work function. The difference of intensity seen in the UPS spectra is likely due to quantum efficiency differences. The lower work function of BaO compared to BaO₂ increases the electron yield (intensity), particularly at high-binding (low-kinetic) energy. Experimental factors such as the irreproducibility of the incident photon flux from the He-I α source, however, cannot be ruled out and prevent quantification of the quantum yield.

The low-kinetic energy cut-off region is expanded in Figure 5b with the abscissa plotted as the difference between photon energy and binding energy, which is the work function. Using the same method, the work function of clean Ag(001) was found to be 4.24 eV, in good agreement with the literature value of 4.22 eV [30]. The work function of Ag(001) decreases when either epitaxial BaO or BaO₂ is deposited. There is some ambiguity in determining the work function of BaO/Ag(001) because of the weak “knee” at the cutoff. Using the cut-off at the knee results in a work function of ~2.5 eV, which is ~1.74 eV below that of the clean Ag(001) surface. A similar treatment of the “knee” was used to measure the work function reduction of SiO_{2.5}/Mo(112) as a function of Li coverage [7]. It should be noted that if, instead, the leading edge of the intense secondary electron tail is extrapolated to zero[14], the work function becomes ~3.0 eV (~1.24 eV below Ag(001)). The work function of the predominantly BaO₂ surface is 3.6 eV, ~0.64 eV lower than that of the pristine Ag(001) substrate. Theoretical calculations predict the work function of Ag(001) to drop from 4.3 eV to approximately 2.0 eV upon BaO deposition [7, 11]. The lowest work function we measure for epitaxial BaO/Ag(001) is 2.5 eV, which is considerably less than that measured for MgO/Ag(001) [13], in qualitative agreement with theoretical predictions. The 0.5 eV difference between calculated and measured values may be due to a variety of factors, including experimental limitations imposed by the mixed BaO and BaO₂ growth mode.

The data presented here suggest an interesting interplay between the structural and electronic properties of the Ba oxide/Ag system. Ba oxide on Ag(001) initially nucleates as 1 ML of BaO,

regardless of the oxygen partial pressure. Additional BaO subsequently nucleates, but BaO₂ also forms. A schematic representation for the BaO overlayer on Ag(001) is shown in Figure 6a. Theoretical modeling predicts that BaO readily accepts excess oxygen to form BaO₂ [31]. Once formed, BaO₂ is highly stable and does not fully decompose until approximately 800 °C [32]. The XPS results presented here are consistent with these predictions and qualitatively confirm the two phases. The UPS results establish that nucleation of predominantly BaO reduces the work function of Ag(001) by ~1.8 eV. The weak intensity knee at ~2.8 eV in the BaO/Ag(001) spectrum (Fig. 5b) may be due to an undetected, partially strained minority component embedded within the largely relaxed majority phase. This conclusion presupposes that epitaxially strained BaO/Ag(001) has the lowest work function, followed by unstrained BaO/Ag(001) and finally BaO₂/Ag(001). One argument against this possibility is that the intensity of this feature in the UPS is relatively insensitive to BaO thickness ranging from ~1 ML to 6 ML-EQ. Previous theoretical work concerning the work function reduction of thin dielectric films on metals predicts that BaO thin films should result in relatively large chemical interactions at the interface with BaO acting as an electron donor. This large charge transfer in combination with the electrostatic compressive effect produces a large work function reduction. However, our results suggest that charge transfer between the BaO and the Ag substrate is negligible. This leads us to conclude that the work function reduction is a result of the electrostatic compressive effect[11] with a minor contribution from surface relaxation.

Fig. 6.

Barium oxide on Ag(111) nucleates as islands of BaO₂ rather than the polar BaO(111) surface. Continued deposition under oxygen-poor conditions produces some BaO along with islands of epitaxial BaO₂. A representation of the BaO₂/Ag(111) is depicted in Figure 6b where Ba atoms occupy a combination of on-top and hollow sites. The oxygen atoms in the first ML largely sit in hollow sites. XPS provides a direct measure of the phase differentiation between the oxide and peroxide phases. The minority BaO may not be crystalline, or may be buried

beneath the BaO₂ islands. Bare patches of the underlying Ag substrate following the epitaxial growth of BaO₂/Ag(111) are also visible by both RHEED and XPS.

IV. Conclusions

We have investigated the epitaxial growth of barium oxide layers on Ag(001) and Ag(111) substrates using molecular beam epitaxy by evaporating Ba metal in an O₂ atmosphere. Deposition on Ag(111) leads primarily to oriented BaO₂(111) islands, presumably to avoid the formation of polar BaO(111), and leaves a fraction of the substrate uncovered. In contrast, deposition on Ag(001) is initiated by the formation of 1 ML of BaO, followed by BaO₂ epitaxial island nucleation (Stranski-Krastanov growth). Growth of BaO on Ag(001) can be driven toward BaO₂ by depositing at higher substrate temperature and using higher O₂ flux. Measured work functions range from 3.6 eV when BaO₂ dominates to 2.5 eV when BaO dominates on Ag(001). There is no detectable charge transfer from the Ba oxide films to the Ag substrates, suggesting that the observed work function reduction is purely due primarily to the electrostatic compressive effect[11] with a minor contribution from surface relaxation. The large work function reduction observed for BaO/Ag(001) suggests that alkaline earth metal oxides on metal supports are interesting near-UV photocathode candidates. Furthermore, this study yields insight into the relative contributions to the work function lowering made by BaO and BaO₂, which are most likely both present in all thin films of Ba oxide.

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Figure Captions:

FIG. 1. RHEED patterns taken during the initial stages of Ba oxide growth on Ag(001) (a-d) and Ag(111) (e-h). BaO nucleates and immediately relaxes on Ag(001) up to approximately 1 ML, at which point BaO₂ growth begins. In contrast, BaO₂ is the predominant phase observed on Ag(111). The monolayer-equivalent doses of Ba oxide from top to bottom are 0, 0.5, 1, and 2.

FIG. 2. Line profiles taken from the RHEED patterns in Fig. 1 for (a) clean Ag(001) (red) and ~2 ML-equivalent BaO on Ag(001) (blue), showing primarily relaxed BaO which acts as the wetting layer for subsequent mixed BaO-BaO₂ epitaxial island growth via a SK-like growth mechanism. (b) clean Ag(111) (red) and relaxed BaO₂ (blue). Peaks attributed to Ag(111) reflections are still visible for thicknesses exceeding 8 ML-EQ, indicating primarily Volmer-Weber growth in this orientation.

FIG. 3. Ba 3d_{5/2} (a), O 1s (b), and Ag 3d (c) spectra for 4 ML-EQ of Ba oxide on Ag(001). The nucleation of both BaO and BaO₂ phases can be seen in the core levels for both Ba and O. The Ag 3d_{5/2} peak can be fit very well with one **symmetric** component indicative of minimal electron transfer between film and substrate.

FIG. 4. Ba 3d_{5/2} (a), O 1s (b), and Ag 3d (c) spectra for 4 ML-EQ of Ba oxide on Ag(111). In contrast to growth on Ag(001), initial growth on Ag(111) is dominated by the nucleation of BaO₂, possibly to avoid creation of a polar surface as would occur for BaO(111) formation. Electron transfer between film and substrate is minimal since the Ag 3d_{5/2} core-level can be fit using one **symmetric** component (inset), even though 3D island film morphology may mask this effect.

FIG. 5. (a) Valence band spectra for ~4 ML-EQ for predominantly BaO (blue) and predominantly BaO₂ (red) on Ag(001) showing a greater work function reduction for BaO. (b) Expanded view of the low-kinetic energy cutoff regions. The work function for films comprised primarily of BaO₂ is 3.6 eV, whereas the value for predominantly BaO is 2.5 eV.

FIG. 6. **Potential schematic representation of (a) 2ML BaO/Ag(001) and 2ML BaO₂/Ag(111) in both plan view and lateral view.** The nucleating phase is arranged with both Ba atoms (magenta) and O atoms (red) adjacent to the Ag atoms (blue) for the creation of zero net dipole moment.