Image potential states of ultrathin NiO films: A time-resolved two-photon photoemission study

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Well-ordered ultrathin films of NiO have been prepared on an Ag(001) substrate using molecular beam epitaxy. With the help of angle-resolved two-photon photoemission (2PPE) a series of image potential states (IPS) for film thicknesses of 2–4 monolayers (ML) has been identified. By time-resolved 2PPE, the lifetimes of the first three IPS and their dependence on the oxide film thickness have been determined. While the lifetimes of the (n=1) IPS are all in the range of 27–42 fs, the values for the (n=2) IPS decrease from 85 fs for 2 ML to 33 fs for 4 ML. These differences are discussed in terms of a coupling to the layer-dependent electronic structure of the NiO ultrathin films.

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ported also earlier, we find a layer-by-layer growth for NiO on Ag(001) for thicknesses from 2 ML and beyond. Hence, after calibrating the evaporator it was possible to prepare well-ordered NiO layers with an accuracy of ±10 % in thickness.

A combination of LEED, XPS, and workfunction measurements has been used for calibration of the NiO film thickness. In the monolayer regime, NiO shows a $(2 \times 1)$ structure. It is formed by a uniaxially distorted, nearly planar, quasihexagonal NiO structure. Above 1 ML, the $(2 \times 1)$ structure vanishes and a pseudomorphic $(1 \times 1)$ film is formed. In Fig. 1(a), diffraction patterns of 1–4 ML NiO/Ag(001) are displayed. Intensity profiles along the $\Gamma X$ direction give clear evidence that the $(2 \times 1)$ diffraction spots only appear for the NiO monolayer (Fig. 1(b)). Figure 1(c) depicts the intensity of the $(2 \times 1)$ LEED spots with increasing coverage (left axis). For the closed monolayer, the $(2 \times 1)$ intensity is maximal. The structural transition from a quasihexagonal monolayer to rocksalt-like NiO films starting from 2 ML on leads to the appearance of the $(2 \times 1)$ spots in LEED.

Due to the quasihexagonality, the chemical environment as well as the resulting surface dipole of the NiO monolayer is different from those of thicker films. These issues lead to unique features in photoelectron spectra and to a high workfunction with respect to other coverages. In Fig. 1(d) XP spectra of the Ni $2p$ core level are depicted for NiO films from 1–4 ML thickness. While the spectra for 2 and 4 ML are similar and even bulk-like in shape, the spectrum for 1 ML NiO/Ag(001) differs significantly: The maximum of the Ni $2p_{3/2}$ peak appears with a difference of 1.4 eV at lower binding energy, and the satellite structure is differently shaped in comparison to the spectra for higher coverages. This is in accordance with findings in the literature and can be taken as a marker for this thickness.

In Fig. 1(c) the workfunction is plotted in dependence of the oxide film thickness. A further characteristic for 1 ML NiO/Ag(001) is the relatively high workfunction $\Phi_{\text{ML}} \sim 5.0$ eV which differs strongly from that of clean Ag(001) ($\Phi_{\text{Ag}} \sim 4.5$ eV) and those of thicker films ($\Phi_{\text{NiO}} \sim 4.2...4.4$ eV). Therefore, one can clearly identify one monolayer thick films on the basis of workfunction measurements.

### III. RESULTS

In Fig. 2 2PPE spectra for two different preparations of 2 ML NiO/Ag(001) are depicted for fixed time delays $\Delta t$ between pump (UV) and probe (IR) pulse. The spectra of Fig. 2(a) were obtained directly after film preparation at room temperature (RT) using photon energies of 4.27 eV and 1.68 eV for pump and probe, respectively. Four different features can be found in the spectra for time delays of $\Delta t=0$ and 115 fs. Long-living states dominate the spectrum at $\Delta t=115$ fs which are marked with 1, 2, and 3 in Fig. 2(b). These features correspond to intermediate state energies of 3.78, 4.04, and 4.14 eV (each ±0.05 eV) above the Fermi level. A fourth short-living
feature, tagged with B, is located at 3.91 eV.

The spectra of Fig. 2 (b) were measured after annealing the sample at 540 K. Again, the spectra can be described by four different states at intermediate state energies of 3.75, 4.05, 4.14, and 3.90 eV (B). In contrast to the measurement directly after RT preparation, the spectra are dominated by feature 1 for both time delays $\Delta t$. Due to the reduced pump photon energy of 4.17 eV, state 3 is hardly populated and not visible in the spectra.

Momentum-resolved data (right panel in Fig. 2) reveal a dispersion of the states 1 and 2 with effective masses for the as prepared (annealed) sample of $m_{\text{eff}} = 1.1 (1.02) m_e$ for feature 1 and $0.97 (1.01) m_e$ for feature 2, respectively. This dispersion corresponds to that of a free electron in front of a surface. Therefore, the unoccupied states 1 and 2 are assigned to the (n=1) and (n=2) IPS of the oxide films.

For 3 and 4 ML NiO/Ag(001), similar unoccupied states are found (Fig. 3). The intermediate state energies of the features are 3.79, 4.11 for the first and second IPS and 3.90 eV (B) for 3 ML. They shift to 3.73, 4.02 (1, 2) and 3.89 eV (B) for 4 ML (each $\pm 0.05$ eV). The energetic positions of these unoccupied states differ only slightly from those of the 2 ML states. According to their dispersion (right panel in Fig. 3) with effective masses $m_{\text{eff}}$ of 0.96, 0.95 (feature 1), and 0.99 $m_e$ (feature 2), the states are again assigned to (n=1) and (n=2) IPS, respectively. In addition, one can recognize a short-living feature B as has been seen for 2 ML.

In Table I, these data are summarized together with the measured sample workfunctions $\Phi$. For the as prepared bi-

layer, the workfunction $\Phi$ amounts to 4.18 eV and is about 250 meV lower than for the annealed NiO films with 2-4 ML thickness. This difference is explained according to the Smoluchowski effect by a higher step density for the as prepared NiO film.

In Fig. 4, time-dependent 2PPE intensities for the first three IPS are depicted for the as prepared 2 ML NiO(001) film. The data points are fitted using a rate equation approach (black solid lines). For comparison, the cross correlation curve between pump and probe pulse with a full width at half maximum (FWHM) of 60 fs is also included in Fig. 4. The solid lines describe the experimental data well over two and a half order of magnitude in intensity and yield lifetimes of 30±5, 50±5, and 120±15 fs for the first three IPS.

For the annealed 2 ML film, the lifetimes (Fig. 5) differ significantly from those of the as prepared film. The lifetime of the (n=1) IPS is about 10 fs longer (42±4 fs) whereas the lifetime of the (n=2) IPS has increased by more than 30 fs (85±15 fs). In Fig. 5, a comparison of the time-resolved 2PPE data for 2, 3, and 4 ML (all annealed to 540 K) is presented. The fits yield lifetimes of 27 and 37 fs (each $\pm 4$ fs) for the (n=1) IPS of 3 and 4 ML. The lifetimes of the (n=2) IPS for 3 and 4 ML amount to 44±6 and 33±7 fs, respectively.

IV. DISCUSSION

In Table I, the workfunctions $\Phi$, binding energies $E_B$, effective masses $m_{\text{eff}}$, and lifetimes $\tau$ of the first three IPS are summarized for 2–4 ML NiO(001) on Ag(001). For the annealed NiO layers, the binding energies are in the range of
640–690 (320–390) meV for the first (second) IPS. The difference of 50 meV for the (n=1) IPS and 70 meV for the (n=2) IPS is close to the uncertainty of the measurement. Nevertheless, these variations can be explained by a slight modification of the NiO electronic structure with film thickness.

Compared to the annealed samples, the binding energies of the IPS of the as prepared sample as well as the workfunction are approximately 250 meV lower. In contrast, the energetic positions of the IPS with respect to the Fermi level are almost unchanged for the as prepared as well as the annealed bilayer (cf. Fig. 2). This is interpreted within the concept of the local workfunction. Workfunction measurements average over a large sample area containing flat NiO terraces as well as stepped NiO regions, resulting in a measured global workfunction. Electrons in an IPS are located in front of the flat NiO terraces only. Therefore, they are affected by the local workfunction of the flat NiO regions. Since the intermediate state energies of the IPS do not change for the as prepared and annealed NiO bilayer, the local workfunction does not change for both preparations. Due to an enhanced film quality upon annealing the NiO bilayer, the local workfunction does not change for both preparations. The workfunction of the NiO bilayer for non-momentum conserving scattering which makes it more defect sensitive. The decay times of the (n=2) IPS for non-momentum conserving scattering which makes it more defect sensitive. The decay times of the (n=2) IPS for 2–4 ML NiO/Ag(001) is, therefore, assigned to a stronger coupling to unoccupied NiO thin film states at this specific thickness. The different IPS lifetimes are, therefore, explainable by a slight modification of the electronic structure for 3 ML is slightly changed as compared to that of 2 and 4 ML thick NiO films. This is also substantiated by the different binding energies of the IPS for 3 ML as discussed above.

The decay of the (n=2) IPS behaves differently for the 2–4 ML films. First, one finds again a longer lifetime of the annealed 2 ML film as compared to 2 ML prepared at RT. This is explained by the improved film quality upon annealing. Clearly, the second IPS is even more sensitive to the film quality due to its longer lifetime as compared to the (n=1) IPS. The (n=2) IPS has an additional decay channel into the (n=1) IPS for non-momentum conserved scattering which makes it more defect sensitive. The decay times of the (n=2) IPS for the NiO bilayer are longer than those for the (n=1) IPS. This follows the general trend known from clean metals that the lifetime of an IPS is increased with increasing quantum number $n$.

The relaxation time of electrons from the (n=2) IPS decreases with increasing film thickness. For 4 ML, the lifetime of the (n=2) IPS electrons is even shorter than for electrons excited into the according (n=1) IPS. This differs strongly from the observations on insulating rare-gas layers with negative electron affinity (EA) on metals. For such systems, the dielectric layer acts as a spacer and decouples the IPS from the metal surface. Due to the negative EA, no additional electronic states of the spacer layer are introduced in the energy range of the IPS. Hence, the wavefunctions of the IPS are pushed away from the metal surface. This results in a strong increase of the lifetimes with increasing layer thickness. The
TABLE I. Workfunctions $\Phi$, binding energies $E_B$, effective masses $m_{\text{eff}}$, and lifetimes $\tau$ of the image potential states for 2–4 ML NiO/Ag(001).

| coverage [ML] | $\Phi$ [eV] | $E_B$ [meV] | $m_{\text{eff}}$ [$m_e$] | $\tau$ [fs] | $E_B$ [meV] | $m_{\text{eff}}$ [$m_e$] | $\tau$ [fs] | $E_B$ [meV] | $\tau$ [fs] |
|--------------|-------------|-------------|-----------------|-------|-------------|-----------------|-------|-------------|-------|
| 2 (A)        | 4.18        | 400±100     | 1.10±0.19       | 30±5  | 120±100     | 0.95±0.20       | 50±5  | 40±40       | 120±15|
| 2 (B)        | 4.44        | 690±100     | 1.02±0.12       | 42±4  | 390±100     | 1.01±0.11       | 85±15|            |       |
| 3            | 4.43        | 640±100     | 0.96±0.13       | 27±4  | 320±100     | 1.01±0.11       | 44±6  |            |       |
| 4            | 4.41        | 680±100     | 0.95±0.12       | 37±4  | 390±100     | 0.99±0.18       | 33±7  |            |       |

behavior of NiO films is, in contrast, similar to rare-gas adlayers with EA > 0. For such systems, the energetic position of the IPS is within the conduction band of the rare gas adlayers. Therefore, the wavefunction of the IPS can penetrate the layer. In case of bulk NiO, the conduction band minimum is located at 2.6 eV above $E_F$.\(^{46}\) The IPS of 2–4 ML NiO on Ag(001) have intermediate state energies of 3.7 eV and more and are, therefore, located in the NiO conduction band. Hence, the wavefunctions of the IPS can couple to those of the NiO thin film states. The decrease of lifetimes for the second IPS from 2 ML to 4 ML NiO/Ag(001) is explained by a stronger coupling of the IPS to thin film states due to an increase of the density of NiO states with increasing film thickness in the energy region of the IPS.

For all prepared oxide films, the feature B occurs at an intermediate energy of 3.9 eV. This state belongs to an electronic transition caused by the silver substrate and is not discussed further here.

V. CONCLUSIONS

We have investigated the image-potential states for NiO(001) ultrathin films of 2–4 ML on Ag(001) by means of angle- and time-resolved 2PPE. The first three IPS were identified via their parabolic dispersion and their relatively long lifetimes. The decay of the IPS depends strongly on the film quality. Compared to a bilayer NiO/Ag(001) prepared at RT, an annealed 2 ML film yield a factor of 1.3 and 1.7 longer lifetimes of the first and second IPS, respectively. For the first IPS the lifetimes are in the range of 27–42 fs and differ only slightly for annealed NiO films with 2–4 ML thickness. In contrast, the lifetimes of the second IPS decrease with increasing film thickness from 85 fs (2 ML) to 33 fs (4 ML). This is explained by the introduction of additional NiO thin film states in the energy range of the IPS. Therefore, electrons in the IPS decay faster due to an increased coupling to these states.

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1. K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, and W. Steimann, “Two-photon photoemission via image-potential states,” Phys. Rev. Lett. 55, 300–303 (1985).
2. S. Schuppler, N. Fischer, Th. Fauster, and W. Steimann, “Bichromatic two-photon photoemission spectroscopy of image potential states on Ag(100),” Appl. Phys. A, Appl. Phys. A 51, 322–326– (1990).
3. R.W. Schoenlein, J.G. Fujimoto, G.L. Eesley, and W. Capehart, “Femtosecond photoemission studies of image potential and electron dynamics in metals,” in Laser Optics of Condensed Matter, edited by Elsa Garmire, Alexei Maradudin, and Karl Rebane (Springer US, 1991) pp. 71–82.
4. T. Fauster and W. Steimann, “Two-photon photoemission spectroscopy of image states,” in Electromagnetic Waves: Recent developments in research., edited by P. Halevi (Elsevier, 1995).
5. I. L. Shumay, U. Höfer, Ch. Reuß, U. Thomann, W. Wallauer, and Th. Fauster, “Lifetimes of image-potential states on Cu(100) and Ag(100) measured by femtosecond time-resolved two-photon photoemission;” Phys. Rev. B 58, 13974–13981 (1998).
6. A. Schäfer, I. L. Shumay, M. Wiets, M. Weinelt, Th. Fauster, E. V. Chulkov, V. M. Silkin, and P. M. Echenique, “Lifetimes of unoccupied surface states on Pd(111),” Phys. Rev. B 61, 13159–13163 (2000).
7. S. Link, H.A. Dür, and W. Eberhardt, “Lifetimes of image-potential states on the Pt(111) surface probed by time-resolved two-photon photoemission spectroscopy,” Appl. Phys. A, Appl. Phys. A 71, 525–528– (2000).
8. M. Marks, C. H. Schwab, K. Schubert, J. Güdde, and U. Höfer, “Quantum-beat spectroscopy of image-potential resonances,” Phys. Rev. B 84, 245402– (2011).
9 D. F. Padowitz, W. R. Merry, R. E. Jordan, and C. B. Harris, “Two-photon photoemission as a probe of electron interactions with atomically thin dielectric films on metal surfaces,” Phys. Rev. Lett. 69, 3583–3586 (1992).
10 M. Wolf, E. Knoesel, and T. Hertel, “Ultrafast dynamics of electrons in image-potential states on clean and Xe-covered Cu(111),” Phys. Rev. B 54, R5295–R5298 (1996).
11 Ch. Reuß, I. L. Shumay, U. Thomann, M. Kutschera, M. Weinelt, Th. Fauster, and U. Höfer, “Control of the dephasing of image-potential states by CO adsorption on Cu(100),” Phys. Rev. Lett. 82, 153–156 (1999).
12 W. Berthold, F. Rebentrost, P. Feulner, and U. Höfer, “Influence of Ar, Kr, and Xe layers on the energies and lifetimes of image-potential states on Cu(100),” Applied Physics A, Appl. Phys. A 78, 131–140. (2004).
13 J. Güdße and U. Höfer, “Femtosecond time-resolved studies of image-potential states at surfaces and interfaces of rare-gas adlayers,” Prog. Surf. Sci. 80, 49–91 (2005).
14 A. Hotzel, “Electronic dynamics of image potential states in weakly bound adsorbate layers: A short review,” Dynamics of Electron Transfer Processes at Surfaces, Prog. Surf. Sci. 82, 336–354 (2007).
15 A. Damm, K. Schubert, J. Güdße, and U. Höfer, “Observation of the transition from image-potential states to resonances on argon-covered Cu(111) and Ag(111) by time-resolved two-photon photoemission,” Phys. Rev. B 80, 205425– (2009).
16 N.-H. Ge, C. M. Wong, and C. B. Harris, “Femtosecond studies of electron dynamics at interfaces,” Accounts of Chemical Research, Acc. Chem. Res. 33, 111–118 (1999).
17 K. J. Gaffney, A. D. Miller, S. H. Liu, and C. B. Harris, “Femtosecond dynamics of electrons photoionized into organic semiconductors at aromatic-metal interfaces,” The Journal of Physical Chemistry B, J. Phys. Chem. B 105, 9031–9039 (2001).
18 X.-Y. Zhu, “Electronic structure and electron dynamics at molecule-metal interfaces: implications for molecule-based electronics,” Surf. Sci. Rep. 56, 1–83 (2004).
19 P.S. Kirchmann, P.A. Loukakos, U. Bovensiepen, and M. Wolf, “Ultrafast electron dynamics studied with time-resolved two-photon photoemission: intra- and interband scattering in c$_2$f$_6$/Cu(111),” NJP 7, 113– (2005).
20 E. Varene, I. Martin, and P. Tegeder, “Optically induced inter- and intrafacial electron transfer probed by two-photon photoemission: electronic states of sexithiophene on Au(111),” The Journal of Physical Chemistry Letters, J. Phys. Chem. Lett. 2, 252–256 (2011).
21 P.M. Echenique, R. Berndt, E.V. Chulkov, Th. Fauster, A. Goldmann, and U. Höfer, “Decay of electronic excitations at metal surfaces,” Surf. Sci. Rep. 52, 219–317 (2004).
22 S. S. Tsirkin, A. G. Borisov, and E. V. Chulkov, “Green’s function approach to the lifetimes of image potential resonances at metal surfaces,” Phys. Rev. B 88, 035449– (2013).
23 D. C. Marinica, C. Ramsay, A. G. Borisov, D. Teillet-Billy, J. P. Gauyaqc, W. Berthold, P. Feulner, and U. Höfer, “Effect of an atomically thin dielectric film on the surface electron dynamics: Image-potential states in the Au/Cu(100) system,” Phys. Rev. Lett. 89, 046802– (2002).
24 P.M. Echenique, J.M. Pitarke, E.V. Chulkov, and A. Rubio, “Theory of inelastic lifetimes of low-energy electrons in metals,” Chem. Phys. 251, 1–35 (2000).
25 K. Onda, B. Li, and H. Petek, “Two-photon photoemission spectroscopy of TiO$_2$(110) surfaces modified by defects and O$_2$ or H$_2$O adsorbates,” Phys. Rev. B 70, 045415– (2004).
26 W. A. Tisdale, M. Muntwiler, D. J. Norris, E. S. Aydil, and X.-Y. Zhu, “Electron dynamics at the ZnO(10 – 10) surface,” J. Phys. Chem. C 112, 14682–14692 (2008).
27 K. Takahashi, K. Ishibashi, Y. Kurashishi, M. Imamura, J. Azuma, and M. Kamada, “Time-resolved two-photon photoemission study of silicon surface at initial stage of oxidation,” Appl. Surf. Sci. 267, 154–158 (2013).
28 J.-C. Deinert, D. Wegkamp, M. Meyer, C. Richter, M. Wolf, and J. Stühler, “Ultrafast exciton formation at the ZnO(10$ar{1}$0) surface,” Phys. Rev. Lett. 113, 057602– (2014).
29 K. Duncker, M. Kiel, and W. Widdra, “Momentum-resolved lifetimes of image-potential states on Ag(001),” Surf. Sci. 606, 87–90 (2012).
30 K. Marre and H. Neddermeyer, “Growth of ordered thin films of NiO on Ag(100) and Au(111),” Surf. Sci. 287, 995–999 (1993).
31 T. Bertrams and H. Neddermeyer, “Growth of NiO(100) layers on Ag(100): Characterization by scanning tunneling microscopy,” in J. Vac. Sci. Technol. B, Vol. 14 (AVS, 1996) pp. 1141–1144.
32 I. Sebastian, T. Bertrams, K. Meinel, and H. Neddermeyer, “Scanning tunneling microscopy on the growth and structure of NiO(100) and CoO(100) thin films,” Faraday Discuss. 114, 129–140 (1999).
33 A. Dhaka, D. Sander, H.L. Meyerheim, K. Mohseni, E. Soyka, J. Kirschner, W. A. Adeagbo, G. Fischer, A. Ernst, and W. Herget, “Stress and structure at the NiO/Ag(001) interface,” Phys. Rev. B 84, 195441 (2011).
34 M. Caffio, B. Cortigiani, G. Rovida, A. Attrei, and C. Giovanardi, “Early stages of NiO growth on Ag(001): A study by LEIS, XPS, and LEED,” J. Phys. Chem. B 108, 9919–9926 (2004).
35 M. Caffio, A. Attrei, B. Cortigiani, and G. Rovida, “STM study of the nanostructures prepared by deposition of NiO on Ag(001),” J. Phys.: Condens. Matter 18, 2379– (2006).
36 S. Großer, C. Hagendorf, H. Neddermeyer, and W. Widdra, “The growth of thin NiO films on Ag(001) studied by scanning tunneling microscopy and spectroscopy,” Surf. Interface Anal. 40, 1741–1746 (2008).
37 S. Großer, Wachstum und lokale elektronische Struktur von ultradünnen NiO- und CoO-Schichten auf einer Silberoberfläche, Ph.D. thesis, Martin-Luther-Universität Halle-Wittenberg (2008).
38 M. Caffio, B. Cortigiani, G. Rovida, A. Attrei, C. Giovanardi, A. di Bonavia, and S. Valeri, “Ultrathin nickel oxide films grown on Ag(001): a study by XPS, LEIS and LEED intensity analysis,” Surf. Sci. 531, 368–374 (2003).
39 D. Alders, F. C. Voogt, T. Hibma, and G. A. Sawatzky, “Non-local screening effects in 2p x-ray photoemission spectroscopy of NiO(100),” Phys. Rev. B 54, 7716–7719 (1996).
40 L. Sangalelli, L.E. Depero, and F. Parmigiani, “On the non-local screening mechanisms in the 2p photoelectron spectra of Nio and La$_2$NiO$_4$,“ Solid State Commun. 103, 421–424 (1997).
41 R. Smoluchowski, “Anisotropy of the electronic work function of metals,” Phys. Rev. 60, 661–674 (1941).
42 R. Fischer, S. Schuppler, N. Fischer, Th. Fauster, and W. Steinmann, “Image states and local work function for Ag/pd(111),” Phys. Rev. Lett. 70, 654–657 (1993).
43 M. Weinelt, C. Reuß, M. Kutschera, U. Thomann, I.L. Shumay, T. Fauster, U. Höfer, F. Theilmann, and A. Goldmann, “Decay and dephasing of image-potential states due to surface defects and disorder,“ Appl. Phys. B, Appl. Phys. B 68, 377–381– (1999).
44 M. Roth, M. Pickel, W. Jinxiom, M. Weinelt, and Th. Fauster, “Electron scattering at steps: Image-potential states on cu(119),” Phys. Rev. Lett. 88, 096802– (2002).
45 P. M. Echenique and J. B. Pendry, “Existence and detection of rydberg states at surfaces,” J. Phys.-C-Solid State Phys. 11, 2065–2075 (1978).
46 F. Reinert, P. Steinert, S. Hüfner, H. Schmitt, J. Fink, M. Knupfer, P. Sandl, and E. Bertel, “Electron and hole doping in NiO,”
Z. Phys. B 97, 83–93 (1995).