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Reduction induced Fermi level pinning at the interfaces between Pb(Zr,Ti)O₃ and Pt, Cu and Ag metal electrodes

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Abstract.

The interface formation between Pb(Zr,Ti)O₃ and Pt, Cu and Ag was studied using *in situ* photoelectron spectroscopy. A strong interface reaction and a reduction of the substrate surface is observed for all three interfaces as evidenced by the appearance of metallic Pb species. Despite the different work function of the metals, nearly identical barrier heights are found with $E_F - E_{VB} = 1.6 \pm 0.1$ eV, 1.8 ± 0.1 eV and 1.7 ± 0.1 eV of the as-prepared interfaces with Pt, Cu and Ag, respectively. The barrier heights are characterized by a strong Fermi level pinning, which is attributed to an oxygen deficient interface induced by the chemical reduction of Pb(Zr,Ti)O₃ during metal deposition.

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1. Introduction

Lead zirconate titanate $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), as one of the most commonly used ferroelectric materials, has been intensively studied due to its potential application e.g. in dynamic random access memory (DRAM), piezoelectric sensors and actuators [1, 2, 3, 4]. For PZT thin film, the cycling stability, imprint performance and leakage current strongly depend on the used electrode material [5, 6, 7, 8]. Electrical fatigue causes a reduction of polarization with increasing switching numbers and is a severe limitation of device operation. The fatigue phenomenon for PZT thin film is especially pronounced with metal electrodes such as Pt. Different fatigue models and mechanisms have been reviewed by Tangantsev *et al.* [9] and Lou *et al.* [10]. Accumulation of oxygen vacancies at the ferroelectric/electrode interface and/or injection of charge carriers through the interface have been suggested to be related to the fatigue phenomenon. Both effects are directly linked to the PZT/electrode interface properties.

As probably the most crucial feature in electronic devices, the choice of electrode material determines the Fermi level position at the interface, which defines the barrier for electron ($\Phi_{\text{B,n}} = E_{\text{CB}} - E_{\text{F}}$) and hole injection ($\Phi_{\text{B,p}} = E_{\text{F}} - E_{\text{VB}}$). For ideal unpinning interfaces, the Schottky barrier heights should depend on the work function of the electrode material. The position of the Fermi level at PZT interfaces indeed shows a strong dependence on the work function with oxide electrodes [11]. The barrier heights at the PZT/ RuO_2 and PZT/ITO interfaces (ITO = Sn-doped In_2O_3) are determined by photoelectron spectroscopy as $\Phi_{\text{B,p}} = 1.0 \text{ eV}$ and $\sim 2.1 \text{ eV}$, respectively, which is $\sim 70\%$ of the work function difference between RuO_2 ($\phi = 6.1 \text{ eV}$) and ITO ($\phi = 4.5 \text{ eV}$). This suggests a rather weak Fermi level pinning at the interface. Based on tight binding calculations for the quantification of the induced gap states model as outlined by Mönch [12], a significantly stronger Fermi level pinning with only $\sim 30\%$ variation of barrier height with electrode work function has been derived by Robertson and Chen [13].

Only a few absolute numbers for barrier heights of different PZT/metal interfaces are reported in literature. Pintilie *et al.* derived barrier heights of $\Phi_{\text{B,p}} = 1.86 \text{ eV}$, 2.11 eV and 2.21 eV for contacts with Pt, Cu and Ag, respectively [14]. The small variation of barrier height with metal work function [15] suggests a rather strong Fermi level pinning at PZT/metal interfaces, in contrast to the PZT/oxide interfaces. Chen *et al.* have investigated the PZT/Pt interface using *in situ* photoelectron spectroscopy [16]. For the as-deposited interface prepared by magnetron sputtering of Pt onto a contamination-free PZT thin film surface, a Fermi level position of $E_{\text{F}} - E_{\text{VB}} = 1.6 \text{ eV}$ has been found. This value is in excellent agreement with the barrier height derived from Scott *et al.* (1.6 eV [17, 18]) and close to the value of Pintilie *et al.* (1.86 eV [14]).

The interface formation between PZT and Pt is characterized, however, by a chemical decomposition of the PZT substrate, which is evident from the observation of metallic Pb species in the photoelectron spectra [16, 19]. It has been suggested that the decomposition of the substrate is caused by the heat of condensation of the metal atoms during deposition, which can be as high as $\sim 4 \text{ eV}$ [20]. Chemically reactive

interfaces have also been observed during deposition of Cu and Au onto (Ba,Sr)TiO₃ [21]. The chemically reduced PZT substrate surface can be reversibly oxidized and reduced by post-deposition treatments under oxidizing or reducing conditions, which is accompanied by a reversible change of the barrier height from $\Phi_{B,p} = 1.1$ eV (oxidizing conditions) to 2.2 eV (reducing conditions) [16]. It has particularly been observed that the changes may already occur at room temperature. The strong dependence of the barrier height on the chemical state of the interface has also been reported by other groups [22, 23]. The effect is not restricted to PZT/Pt but also observed at other oxide/metal interfaces [24, 25].

During the deposition of oxides on top of PZT no metallic Pb emission was detected in the Pb 4f photoelectron spectra. As these interfaces do not show a strong Fermi level pinning, it is suggested that the Fermi level pinning reported for PZT/metal interfaces [14] is related to the chemical reduction of the interface. In this study the interface formation between Pt, Cu, and Ag with PZT thin films has been investigated using *in situ* X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS). A chemical reduction of PZT is reported for all three interfaces. In addition, the barrier height depends only weakly on the metal work function. The results therefore provide strong support that the chemical reaction at the interface is the origin of Fermi level pinning of as-deposited PZT/metal interfaces.

2. Experimental

The experiments were performed using the integrated surface analysis and preparation system DAISY-MAT (DAmstadt Integrated SYstem for MATerial Research), which combines a Physical Electronics PHI 5700 multitechnique surface analysis system with several deposition chambers via an ultrahigh vacuum sample transfer [16]. At room temperature Pt, Ag and Cu, respectively, were incrementally deposited onto clean PZT substrates. After each deposition the sample was examined by XPS using a monochromatic Al K _{α} photon source, which provides a typical resolution of ~ 0.4 eV, as determined by the gaussian broadening of the Fermi edge of a metallic Ag reference sample. Binding energies are given with respect to the Fermi edge emission of the same reference with a typical accuracy of < 100 meV. Due to the low film thickness of the PZT films of 50 nm, no strong charging of the sample during photoemission measurement was observed. All XP spectra were recorded using a takeoff angle of 45°. Ultraviolet photoelectron spectra were excited with He discharge lamp ($h\nu = 21.2$ eV) and recorded in normal emission with a -1.5 eV sample bias.

The PZT thin films were prepared by pulsed laser deposition using a KrF 248 nm excimer laser with a repetition rate of 10 Hz and an energy density of 1.8 J/cm². Platinized Si wafers (Inostek) were used as substrates. The temperature during PZT deposition was set to 650 °C and the oxygen pressure was kept at 30 Pa. A PZT target with a Zr/Ti ratio close to the morphotropic composition (52/48) was used for deposition. The Zr/Ti ratio is maintained during deposition as verified by chemical

composition analysis using XPS. In order to obtain contamination-free surfaces prior to metal deposition, the PZT thin films were heated to 400 °C in 0.5 Pa oxygen for 1 h, which has effectively been used for cleaning other oxide surfaces [24, 26]. Platinum and copper were deposited onto clean PZT thin films using radio-frequency magnetron sputtering at room temperature from 2" targets with a power of 5 W, an Ar gas pressure of 0.5 Pa and a substrate to target distance of 10 cm. The deposition rates estimated from the attenuation of the substrate emission lines are ~ 5 nm/min for Pt and ~ 1.6 nm/min for Cu, respectively. Silver was evaporated from a temperature controlled effusion cell using an Al₂O₃ crucible. The vacuum during metal deposition was below 10^{-6} Pa. The evaporation rate is ~ 1.5 nm/min.

3. Results and Discussion

Typical XPS survey spectra recorded during the course of copper deposition onto PZT are presented in Figure 1. The as-prepared film shows emissions from Pb, Zr, Ti, O and C. The C emission is attributed to adsorbed hydrocarbon species with a representative binding energy of 285 eV. No significant carbonate species are observed at higher binding energy in the C 1s spectrum. After heating the sample at 400 °C in 0.5 Pa oxygen for 1 h, no emissions related to carbon are detected. The sample remained free of (carbon) contaminations during the whole experiment.

During stepwise deposition of Cu, the substrate emission lines are attenuated and the Cu emission intensity increases. After deposition of ~ 18 nm of Cu the Zr 3d, Ti 2p and O 1s lines are completely attenuated. In contrast, the Pb emissions can still be recorded after 36 nm of copper deposition and the Pb emission intensity does not change from 18 to 36 nm Cu film thickness. This indicates that metallic Pb is floating on the surface of the growing Cu film.

The inset shows the valence band spectra including secondary electron cutoff recorded with ultraviolet photoelectron spectroscopy using HeI, corresponding to a work function of $\phi = E_{\text{vac}} - E_F = 4.7 \pm 0.1$ eV for PZT. The valence band maximum (VBM) position is derived by linear extrapolation of the leading edge of the valence band emission at $E_F - E_{\text{VB}} = 2.1 \pm 0.1$ eV. This value is ~ 400 meV larger than the VBM position derived from the XPS spectra (see inset in Figure 3(b)), which can be attributed to a slight charging of the film, as charging in UPS is typically stronger than in XPS. While charging affects the absolute binding energies of the VBM and the secondary electron cutoff, the shift of both values is identical if the charging is not too large. The ionization potential ($I_P = E_{\text{vac}} - E_{\text{VB}}$) and the electron affinity $\chi = I_P - E_{\text{gap}}$ are not affected in this case and are determined from the UP spectrum as $I_P = 6.8$ eV and with a band gap of 3.4 eV [1] as $\chi = 3.4$ eV. These values compare well with those given by Scott ($\chi = 3.5 \pm 0.2$ eV [1, 17]). It is noted, however, that the ionization potential may depend strongly on surface orientation and surface termination [27, 28] and is therefore a poor quantity for estimating Schottky barrier heights.

X-ray induced Pb 4f and O 1s photoelectron core level spectra of the PZT substrate

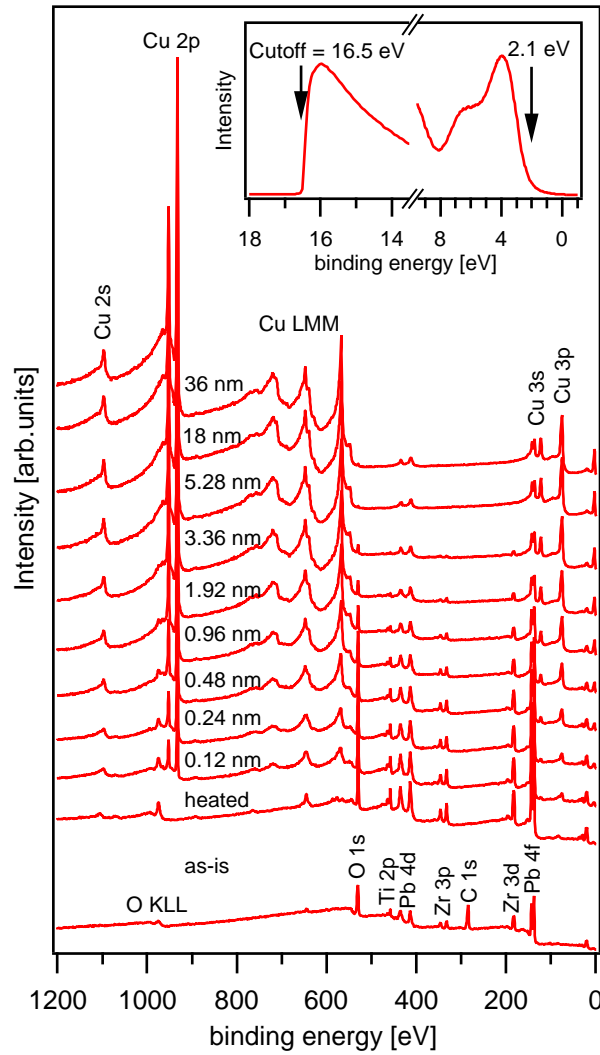


Figure 1. X-ray photoelectron survey spectra recorded during incremental deposition of Cu onto Pb(Zr,Ti)O₃. The thickness of the Cu film after each deposition step is indicated. The inset shows an ultraviolet photoelectron spectrum of a cleaned PZT film.

and Pt 4f, Cu 2p_{3/2} and Ag 3d_{5/2} core levels of the deposited metals recorded in the course of Pt, Cu and Ag deposition are shown in Figure 2. The emissions of Zr 3d and Ti 2p are not shown here, as no changes in line shapes are observed in the course of metal deposition, as already reported in Ref. [16] for the PZT/Pt interface. The binding energies of the Zr 3d and Ti 2p core levels shift in parallel with the oxide Pb 4f component. The Pb 4f emissions of the clean PZT substrates exhibit a single doublet structure, related to oxidized Pb in PZT (Pb^{+II}). Slightly different binding energies of the PZT substrate emissions may be attributed to weak sample charging or to slightly different conditions of the substrate/PZT interface. Different charging of the samples may result from different thickness of the nominally insulating films or from varying substrate conditions during growth of the PZT films.

The constant line shapes and widths of core levels attributed to the PZT substrate,

which are the Zr 3d, Ti 2p and the $\text{Pb}^{+\text{II}}$ 4f emissions, indicate that the formed barriers have a unique value and do not vary along the surface. As the deposited films are polycrystalline in nature due to the polycrystalline substrate used, this indicates that the barrier heights do not depend on interface orientation as also demonstrated recently for the PZT/RuO₂ interface [29].

The deposition of all three metals leads to a partial decomposition of the PZT substrate, as evident from the observation of a metallic Pb component, which is indicated in Fig. 2(a-c) by dashed vertical lines. A metallic Pb component appears at a binding energy of ~ 137 eV and is most pronounced for Cu deposition. The weakest intensity of metallic Pb is observed for Ag deposition. An interface reaction is not expected in the view of bulk thermodynamics as the metal oxides of Pt, Cu and Ag have only low heats of formation. Copper has the largest heat of formation of metal oxide for the studied contact metals. This corresponds with the largest amount of metallic Pb observed during deposition of Cu, suggesting that metal oxide formation contributes to the decomposition of the substrate. Formation of Pt-, Cu- or Ag-oxides is, however, not observed in the XP spectra.

In interface experiments using photoemission, a decomposition of the substrate has been observed even if the contact partners do not react in the bulk [30]. The frequently observed reduction of compound semiconductor substrates in the course of metal deposition has also been related to the condensation energy of the deposited species [31]. This has to be expected particularly for deposition of atomic species, as is the case for magnetron sputtering or thermal evaporation of metals. Rao *et al.* have explicitly calculated the binding energy of Pt on BaTiO₃ to be 4 eV [20], which exceeds the vacancy formation energy in the bulk [32]. As vacancy formation at surfaces is typically less expensive than in the bulk due to the lower coordination number, the reduction of the substrate at the surface becomes even more favourable.

Additional energy gain favoring substrate decomposition may come from the dissolution of substrate metal atoms in the growing metal film. Enthalpies of solution of Pb in Pt, Cu and Ag have been calculated as -16, +23 and +9 kJ/mol, respectively [33]. Intermetallic Pt-Pb phases like Pt₅₋₇Pb [34, 35] and Pt₃₋₄Pb [36] are also believed to serve as nucleation seeds for PZT(111) orientation during growth of PZT on Pt. As an additional term the surface energy of the deposited materials might be lowered by segregation of the substrate species to its surface (surfactant effect).

The evolution of the intensity of the metallic Pb species is not the same for the three metals as also evident from Fig. 2. While the metallic Pb is attenuated with increasing Pt deposition, its intensity saturates in the case of Cu and Ag deposition. The behavior for Cu and Ag is explained by Pb floating on top of the growing metal film, while the metallic Pb remains at the interface or is dissolved in the growing Pt film. The different behavior of the metallic Pb species is in accordance with the different enthalpies of solution of Pb in Pt, Cu and Ag. Lead is expected to dissolve only in Pt while the positive heat of solution with Cu and Ag should result in a segregation of Pb.

The binding energy of Pt 4f_{7/2}, Cu 2p_{3/2} and Ag 3d_{5/2} lines for the thick Pt, Cu,

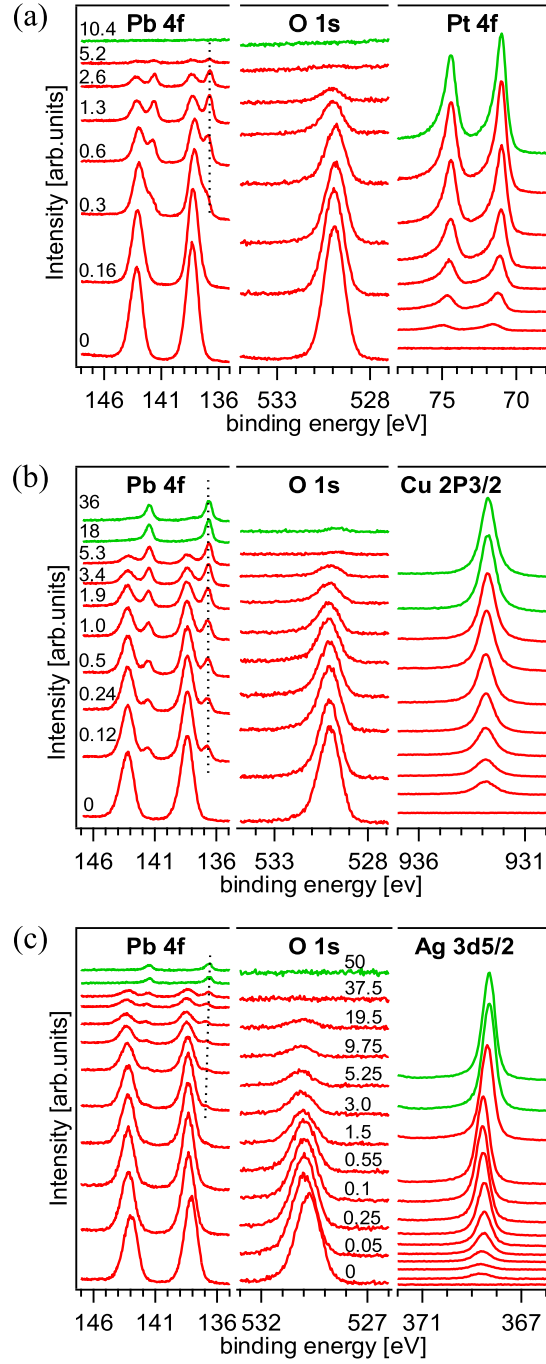


Figure 2. X-ray photoelectron core level spectra of PZT thin films in the course of Pt (a), Cu (b) and Ag (c) deposition. The core level spectra of Ti 2p and Zr 3d are omitted. The dashed lines indicate metallic Pb. The thickness of different deposited metallic films is given in nanometers.

and Ag films are 71.1 eV, 932.7 eV, and 368.3 eV, respectively, which are the same as the binding energies of the clean metals [37]. The binding energy of the Ag emission is slightly higher for lower film thickness, which could be related to island formation of the Ag film [38]. Large binding energy shifts of metals can also be caused by alloy formation as reported e.g. for alloys of Au with In and Ga [39, 40]. Alloy formation may also be the reason for the decreasing binding energy of the metallic Pb component in the case of Ag deposition. It has been argued above, however, that alloying of Pb with Ag is not likely. A third possible explanation for the binding energy shifts of the Ag and the metallic Pb emission is sample charging, which could cause larger binding energies for low metal film thickness. The charging will disappear when a metal film is deposited on the sample, as the film electrically connects the surface of the sample with the sample holder once the film is sufficiently thick, which occurs already after a few nm of deposition [41, 42].

The O 1s core levels are attenuated after the final Pt and Ag deposition but not for the Cu covered sample, where a small signal around 529.7 eV binding energy remains. Such a behavior has also been observed during Cu and Au deposition onto (Ba,Sr)TiO₃ [21]. The oxygen signal after Cu deposition is still observed after complete attenuation of the Pb^{+II}, Ti, and Zr core levels, clearly indicating that it is not related to PZT, as might have been the case e.g. for islands growth of the Cu film. The O 1s signal does not decrease after the final Cu deposition, suggesting that the remaining O 1s comes from oxygen on the surface of the Cu film. Such surface oxygen is noticed only for deposition of Cu, which also leads to the largest amount of metallic Pb. The source of oxygen is therefore attributed to the chemical reduction of the PZT substrate. The absorption of oxygen or water from the vacuum chamber as source for the appearance of an O 1s emission after Cu deposition is not likely, as Cu and Pt were deposited under comparable conditions and oxygen would also adsorb on Pt.

To determine the Schottky barrier heights, the Fermi level positions at the interfaces are required. These are derived from the core level binding energies by subtracting the binding energy difference of the PZT core levels with respect to the PZT valence band maximum of the uncovered substrates. The core level to valence band maximum binding energy difference is constant for a material and should not change during metal deposition if no strong chemical disruption of the substrate occurs [43, 44, 45]. The PZT-related core level emissions, including the oxidic Pb^{+II} 4f component, exhibit parallel shifts during metal deposition for all three interfaces as evident from Figure 3(a-c). Due to the parallel shift of these binding energies, it is safe to attribute them to emissions from structurally intact PZT substrate and hence to shifts of Fermi level position with respect to the PZT valence band maximum. The starting positions of the VBM of the cleaned PZT films are derived from the XPS valence band spectra before metal deposition, which are shown in the insets of Fig. 3. Any charging effect during photoemission of the uncovered PZT films will not affect the barrier height determination, as the deposited metal layer will create a short circuit between the surface and the sample holder. The latter defines the binding energy reference. The Fermi level

equilibration (electrical contact) of the surface and the sample holder is justified by the fact that the binding energies of the core levels of the deposited metals correspond to their reference values. Therefore, the Fermi level is at zero binding energy after metal deposition. The binding energy of the valence band maximum after metal deposition, which is extracted from the binding energy before deposition plus the change of binding energy of the core levels during deposition, corresponds to $E_F - E_{VB}$ at the interface, i.e. the hole Schottky barrier.

As also observed for the Pb 4f emission, the VBM binding energies of the three PZT thin films before metal deposition are slightly different, which may be attributed to different sample charging or to slightly different conditions of the substrate/PZT interface. The Fermi level positions at the interface with the deposited metal are derived from the plots in Fig. 3 for a metal thickness where the shifts of the core level binding energies saturate. The Fermi levels are $E_F - E_{VB} = 1.6 \pm 0.1$ eV, 1.8 ± 0.1 eV and 1.7 ± 0.1 eV at the PZT/Pt, PZT/Cu and PZT/Ag interfaces, respectively. These values directly correspond to the Schottky barrier heights for holes, while the Schottky barrier heights for electrons are calculated using a band gap of 3.4 eV [1] as $E_{CB} - E_F = 1.8 \pm 0.1$ eV, 1.6 ± 0.1 eV and 1.7 ± 0.1 eV, respectively. Considering the experimental uncertainty, the Fermi level at the interface is more or less located at the same position for all three metals. This result is in very good agreement with the similar leakage currents for these materials [14].

The energy band diagrams of the three different PZT/metal interfaces are summarized in Fig. 4. The vacuum level, which is included in Fig. 4, is derived from the work functions of 5.65 eV, 4.65 eV and 4.25 eV for Pt, Cu and Ag, and from an ionization potential of PZT of 6.8 eV, respectively. The possible band bending in the PZT substrate is not included in the graphs, as the absolute Fermi level position in the interior of the films is uncertain due to possible charging effects. Due to the low doping of the PZT films, it is also reasonable to assume that the films are fully depleted. The energetic situation at the investigated PZT/metal interfaces is, however, not affected by this uncertainty as the Fermi level of the deposited metal serves as the binding energy reference. The barrier heights at the interfaces are derived from the XPS measurements described above. The difference in contact potential for the three different metals is mainly compensated by large interface dipole potential drops. These are 0.45 ± 0.1 eV for PZT/Pt, -0.35 ± 0.1 eV for PZT/Cu and -0.84 ± 0.1 eV for PZT/Ag, respectively.

The Schottky barrier heights may be modified by post-deposition treatments, as previously demonstrated for the PZT/Pt interface [16, 22, 23]. It is currently not clear if such modification is also possible for Cu and Ag contact materials, as these exhibit a different chemical structure of the interface. This is related to the different solution enthalpies of Pb in the deposited metals. While Pb can dissolve in Pt and therefore remain close to the interface, it is not dissolved in Cu and Ag and hence segregates to the surfaces of these films. The variation of barrier height observed with Pt contacts is accompanied by an increase/decrease of the metallic Pb species [16, 22, 23]. This suggests that the insensitivity of the barrier height on the metal work function is related

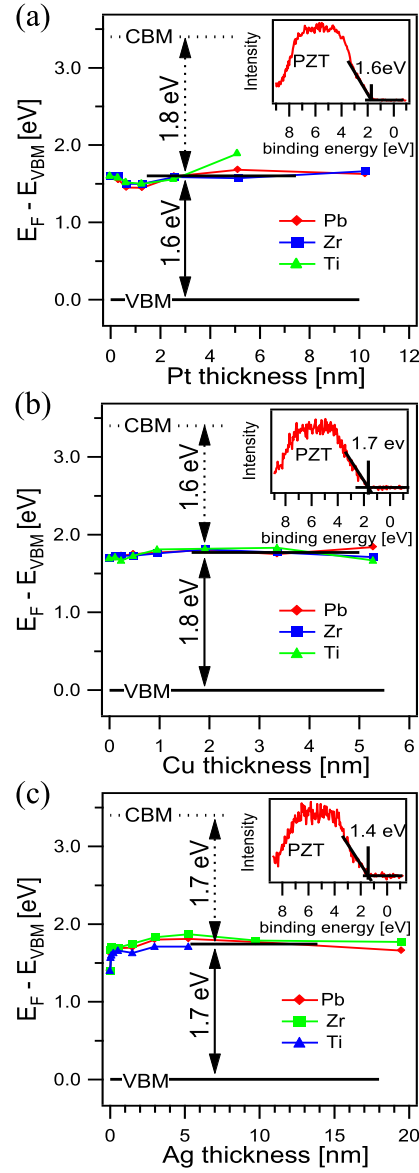


Figure 3. Evolution of the PZT core level lines with increasing Pt (a), Cu (b) and Ag (c) thickness. The distance between core level lines and VBM has been subtracted. The Schottky barrier height for holes $\Phi_{B,p}$ corresponding to the distance between Fermi level E_F and the valence band maximum E_{VBM} , amounts to 1.6 ± 0.1 eV for PZT/Pt interface, 1.8 ± 0.1 eV for PZT/Cu interface and 1.7 ± 0.1 eV for PZT/Ag interface as determined from the saturation of the core level binding energy shift. The PZT band gap was taken as 3.4 eV [1]. VBM and CBM refer to the band edges of PZT. The insets indicate the x-ray photoelectron valence band spectra of the uncovered PZT films used for each interface formation experiment.

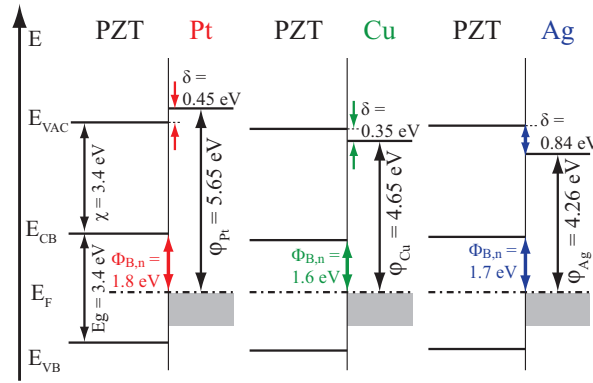


Figure 4. (Color online) band diagram of PZT/ Pt, PZT/Cu and PZT/Ag interfaces containing interface states reflected by the dipole potential δ . The electron affinity $\chi = 3.4$ eV of the cleaned PZT thin film was derived from the UPS measurement and an energy gap of 3.4 eV [1]. Considering the Schottky barrier heights for electrons $\Phi_{B,n}$ at the interfaces and taking the work function of 5.65 eV, 4.65 eV and 4.26 eV for Pt, Cu and Ag [14], respectively, into account, the dipole potential δ can be derived from the discontinuity of the vacuum level E_{VAC} at the interfaces. E_{CB} , E_F and E_{VB} refer to conduction band, Fermi level and valence band of PZT, respectively.

to the decomposition of the substrate. There are several processing options where the substrate decomposition may be avoided: (i) condensation of atomic species of metals might be avoided by deposition from solutions, like (electro-)chemical or metal pastes, or from gaseous compounds (metal-organic); (ii) direct contact of the deposited species with the bare PZT surface might be avoided by covering the surface with sub-nanometer thick buffer layer before metal deposition; (iii) post-deposition treatments like firing in ambient conditions as typically performed for ceramic actuators. All such treatments should lead to a different reactivity at the interface and therefore to different barrier heights and leakage currents.

Fermi level pinning is a well known phenomenon for semiconductor interfaces, which is particularly pronounced for covalently bonded semiconductors like Si or III-V compounds [46]. The Fermi level pinning is related to induced gap states, which occur at semiconductor interfaces due to the wave function matching leading to an exponentially decaying wave function in the semiconductor energy gap [47, 48]. For a high density of induced gap states, the Fermi level at the interface is pinned close to the charge neutrality level of the induced gap states [49], which has been derived by evaluating branch point energies or dielectric midgap energies [12, 50, 51]. Charge neutrality levels for high permittivity oxides have been calculated by Robertson and Chen [13]. The levels for PbTiO_3 and PbZrO_3 are given as $E_{CNL} - E_{VB} = 1.9$ and 2.6 eV, respectively. The former corresponds well with the Schottky barrier heights determined for PZT in this work. The samples used in the experiments, however, have a Zr/Ti ratio of nearly 0.5. If the charge neutrality level scales linearly with the composition, an $E_{CNL} - E_{VB} \approx 2.35$ eV is estimated based on the values of Robertson and Chen. This is significantly higher than the observed Fermi level position at the three interfaces.

Extrinsic defects can considerably affect the barrier heights [16, 24, 25, 52, 53]. It is therefore only reasonable to compare charge neutrality levels with experimental Schottky barrier heights for interfaces with low concentrations of extrinsic defects. As the defects are related to a chemical reduction of the interface, it is likely that these are related to oxygen deficiency. Hence, the lowest defect concentrations are expected for most oxidizing conditions, which consistently leads to a downward shift of the Fermi energy at the interface [16, 24, 25], corresponding to a lowering of the hole Schottky barrier. The lowest Fermi level position observed at the PZT/Pt interface is $E_F - E_{VB} = 1.1$ eV [16], which is significantly lower than the charge neutrality level calculated by Robertson and Chen [13]. Due to the large deviation between the charge neutrality level and the Schottky barrier height for nearly defect-free interfaces, it is suggested that Fermi level pinning by induced gap states is not pronounced for PZT/metal interfaces. This is in agreement with the large variation of Schottky barrier heights of PZT with RuO_2 ($\phi = 6.1$ eV) and Sn-doped In_2O_3 ($\phi = 4.5$ eV) [11], where oxygen deficiency is not expected to play a role. The observed Fermi level pinning at PZT/metal interfaces is consequently ascribed to extrinsic defects at the interface. Due to the observed chemical reduction of the PZT, oxygen vacancies are the most likely candidates for these defects.

4. Summary and Conclusion

The interface formation between contamination-free surfaces of PZT thin films with Pt, Cu and Ag has been studied using photoelectron spectroscopy with *in situ* metal deposition. The metals are deposited either by magnetron sputtering or by thermal evaporation. Metal atoms are thus the dominant gas phase species in the deposition process. Their condensation on the surface results in a chemical decomposition of the PZT substrate, as observed during deposition of all three metals. This is evident from the observation of a metallic Pb species, which is most pronounced for deposition of Cu.

The Schottky barrier heights of PZT with Ag, Cu and Pt are the same within the experimental uncertainty and are derived as $E_F - E_{VB} = 1.7 \pm 0.1$ eV. For a band gap of 3.4 eV, this corresponds to a midgap Fermi level position and nearly identical Schottky barrier heights for electrons and holes. As Schottky emission often dominates the leakage current within PZT/metal contacts, a similar magnitude of leakage current is expected. Pintilie *et al.* [14] found that the leakage current is largely insensitive to the work function of the top metal electrodes, which is in very good agreement with the similarity of the Schottky barrier heights derived from the photoemission measurements presented here.

The observed Fermi level pinning at PZT/metal interfaces is attributed to oxygen vacancies at the interface, which are induced by the chemical reaction. Fermi level pinning by induced gap states, which is important for more covalently bonded semiconductors, is less important for the PZT/metal interfaces.

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