The electromechanical parameters at the interface of a ferroelectric material in contact to a metal play an important role in novel ferroelectric devices such as FeRAM\textsuperscript{1} or future ferroelectric solar cells\textsuperscript{2}. A promising material for such devices is the oxide relaxor 72\% Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} - 28\% PbTiO\textsubscript{3} (PMN-PT) due to its high remanent polarization (P\textsubscript{r} = 45 \mu C/cm\textsuperscript{2}) at a low coercive field (E\textsubscript{c} = 2 kV/cm) and its very high piezoelectric coefficients\textsuperscript{3}. As a typical metallic perovskite oxide, we used epitaxial grown SrRuO\textsubscript{3} thin film electrodes in our study. Employing photoelectron spectroscopy with high kinetic energies at beamline 4 and beamline 9 (PETRA III), we particularly studied the influence of the electrical polarization and variable strain in the ferroelectric material on the band alignment at the metal-ferroelectric interface.

In the investigated samples the ferroelectric material is sandwiched between two metal electrodes, as shown in Fig. 1(a). The electrically grounded top electrode consists of a 6 nm-thin SrRuO\textsubscript{3} film. Since high photon energies (Experimental station ASPHERE III at P04: 1.6 keV, P09: 6 keV) are used, the photoelectrons emitted from PMN-PT have high kinetic energies and can easily penetrate the top electrode. The bottom electrode consists of a thick Au film and is connected to a variable voltage source so that electric fields can be applied to the ferroelectric crystal \textit{in situ} during the photoemission measurements.

In order to study the impact of the PMN-PT polarization on the band alignment, we measured the Pb 4f and Sr 3d core levels for different electric fields (see Fig. 1(b)). The measurement sequence was as follows: +15 kV/cm, 0 kV/cm, −15 kV/cm, and 0 kV/cm. The Sr 3d emissions originate from the top metallic electrode and, hence, are not influenced by the applied electric field. In contrast, the Pb 4f emissions originating from PMN-PT vary with the applied potential (red and blue curve) and...
Figure 2: (a) Pb 4f and Sr 3d HAXPES spectra as a function of photoelectron escape angle / probing depth. (b) Color coded Pb 4f\textsubscript{7/2} core-level spectra for different electric fields; each horizontal line represents one spectrum. In this measurement a Au top electrode was used, but samples with SrRuO\textsubscript{3} top electrodes showed the same behavior (P09, $h\nu = 6$ keV).

show hysteretic behavior (black curves at zero field). The observed variation of the binding energy for several PMN-PT core levels can be ascribed to an additional potential at the metal-ferroelectric interface. Since the kinetic energies of the Pb 4f photoelectrons are dependent on the history of the applied electric field, we can relate the effect to the polarization of the ferroelectric PMN-PT. If the polarization is pointing upwards, the photoelectrons lose kinetic energy upon crossing the metal-ferroelectric interface, whereas they gain kinetic energy, if the polarization is pointing downwards. At higher temperatures (425 K) the PMN-PT is in the cubic paraelectric phase and, thus, the Pb 4f photoelectrons are not influenced by a macroscopic polarization (green curve), and their energies can be measured at intermediate values between the two polarization states. The shift of the PMN-PT core levels induced by the polarization is about 500 meV.

In order to study the depth distribution of the polarizations states during the polarization reversal, we chose the potential in such a way, starting from up polarization, that the two features corresponding to up and down polarization are simultaneously measured in one spectrum (see Fig. 2(a)). The spectral changes upon varying the photoelectron detection angle (with respect to normal emission) show that the topmost PMN-PT layers near the metal-ferroelectric interface switch first to the down polarization state.

By slowly changing the electric field in small steps a switching of the polarization could be avoided even at fields higher than the coercive field and the up polarization state could be preserved for both electric field directions. As shown in Fig. 2(b), the Pb 4f\textsubscript{7/2} binding energy increases with the absolute value of the applied electric potential, but independent of the field direction. Supported by the very high piezoelectric coefficients, this shift can be related to strain variation in the PMN-PT. At a field of $\pm 15$ kV/cm the strain-induced energy shift is determined to about 200 meV.

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