Surface and interface effects on the electronic and magnetic properties of $NiCo_2O_4$ thin films

A. Subedi,[1] B. Giri,[1] D. Yang,[1] A. T. N'Diaye,[2] T. Komesu,[1] X. Xu,[1] P. Dowben[1]
[1] Department of Physics and Astronomy Theodore Jorgensen Hall 855 North 16th Street University of Nebraska-Lincoln Lincoln, NE 68588-0299, U.S.A.
[2] Advanced Light Source, Berkeley, CA 94720, U.S.A

The surfaces of epitaxial complex oxide thin films could differ chemically from its bulk. The distinctly different surface can lead to different surface electronic and magnetic properties compared to the bulk properties of the thin films. Using angle-resolved x-ray photoelectron spectroscopy (ARXPS) of the $NiCo_2O_4$ (NCO) thin films, NCO thin film surfaces are found to be Ni-rich and there exist surface-to-bulk core level shifts in binding energies of the Ni $2p_{3/2}$ and Co $2p_{3/2}$ core levels [1, 2]. While the Ni-rich conducting NCO thin film surface undergoes irreversible metallic to non-metallic (dielectric) phase transition, the highly reduced surface of the NCO thin film undergoes reversible phase transition from highly dielectric to much diminished dielectric (or highly enhanced metallic) character with temperature [2]. We have proposed a modified Arrhenius-type model for the core level binding energy change with temperature in x-ray photoelectron spectroscopy (XPS) of dielectric oxide thin films, and activation energies for thermal stimulations of the carriers are thus estimated [2]. Spin-polarized inverse photoemission spectroscopy (SPIPES) and angle-resolved x-ray magnetic circular dichroism (XMCD) of Ni-rich NCO thin film show that the surface spin moments of the film are canted, although the same film in the bulk is known to possess perpendicular magnetic anisotropy (PMA). When a thin platinum (Pt) layer was deposited on the NCO film, the spin moment canting at the interface of Pt/NCO increased dramatically, leading to significantly different spin ordering at the interface compared to the bulk spin ordering (PMA) of the NCO thin film. The reversibility in electronic phase transition can ultimately lead to two controlled, programmable and non-volatile electronic phase states, whereas spin-canting surfaces and interfaces make NCO thin films interesting for spintronics.

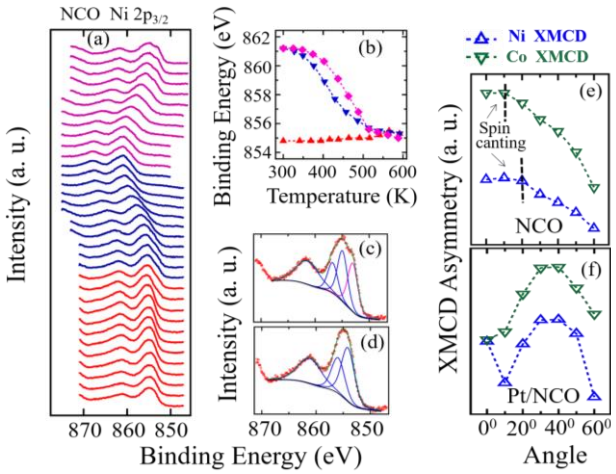

Figure 1. (a) Temperature-dependent Ni $2p_{3/2}$ XPS spectra of a NCO thin film and (b) corresponding measured binding energies. (c) Ni $2p_{3/2}$ XPS spectra of highly reduced NCO surface which undergoes reversible non-metal (dielectric) to metal transition (blue and pink spectra (a) and markers (b)). (d) Ni $2p_{3/2}$ XPS spectra with surface, bulk, and satellite components (blue) for conducting NCO surface (red spectra (a) and markers (b)). XMCD magnetic asymmetries for the (e) surface of NCO and (f) interface of Pt/NCO at Ni and Co absorption edges. Angle is the angle of incident photon w.r.t. surface normal of the sample.

[1] **A. Subedi**, D. Yang, W. K. Chin, B. Tamang *et al.*, J. Phys.: Condens. Matter **36**, 285001 (2024).
[2] **A. Subedi**, D. Yang, X. Xu, and P. A. Dowben, J. Phys. D: Appl. Phys., in press, (2024).
[https://doi.org/10.1088/1361-6463/ad5aa8]

Supplementary materials:

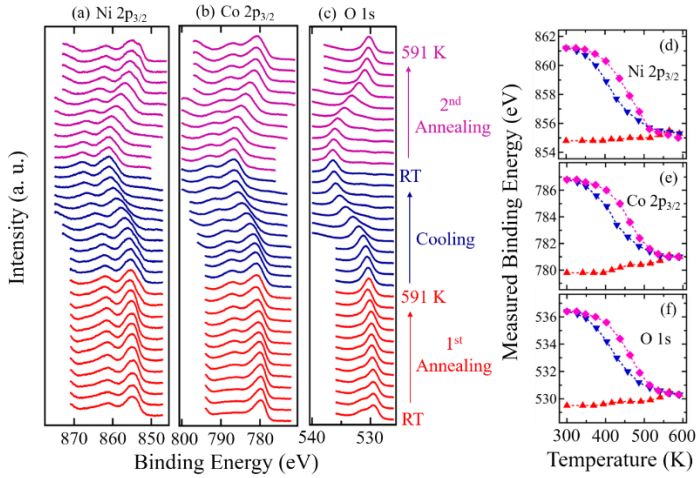

FIG. 1. The temperature-dependent x-ray photoelectron spectroscopy (XPS) core level spectra ((a)-(c)) and corresponding peak positions (binding energies) ((d)-(f)) of $NiCo_2O_4(111)$ thin film in ultra-high vacuum [1]. RT is room temperature.

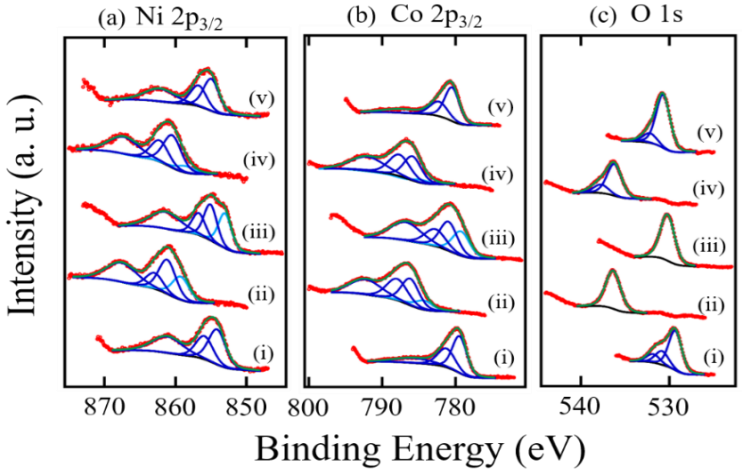

FIG. 2. The XPS of $NiCo_2O_4(111)$ thin film after different annealing and oxygen exposure treatments. It is found that conducting (reduced and insulating) $NiCo_2O_4(111)$ surface undergoes irreversible (reversible) metallic to non-metallic phase transition with temperature, and original metallic character of the $NiCo_2O_4(111)$ surface is restored when the $NiCo_2O_4(111)$ thin film is annealed in ambient or sufficient oxygen [1].

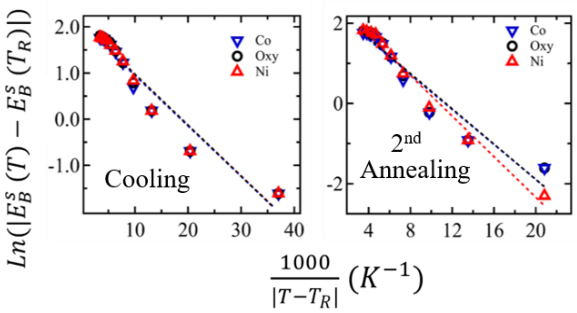

FIG. 3. Shown are the plots, using temperature-dependent XPS core level binding energies ($E_B^S(T)$) of insulating $NiCo_2O_4(111)$ thin film, for a modified Arrhenius-type model [1].

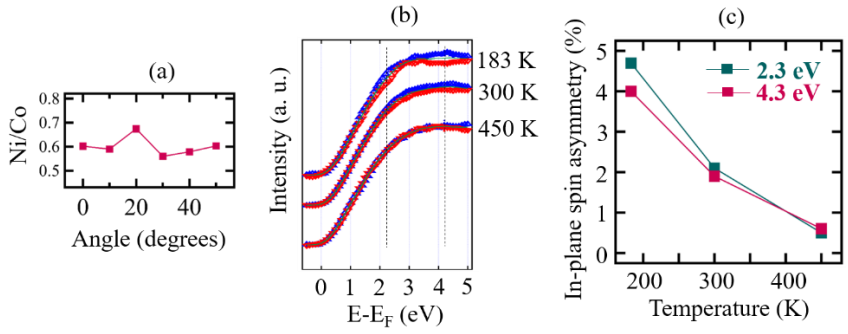

FIG. 4. (a) Concentration ratio of Ni to Co for the $NiCo_2O_4$(001) thin film surface, estimated using angle-resolved XPS, showing that the ratio Ni/Co is well above 0.5. The $NiCo_2O_4$(001) thin film surface, therefore, is Ni-rich, as in the case for $NiCo_2O_4$(111) thin film surfaces [1, 2]. Angle is photoelectron emission angle with respect to the surface normal of the sample. (b) Spin-polarized inverse photoemission spectroscopy (SPIPES) of $NiCo_2O_4$(001) thin film surface, showing (c) in-plane spin polarization of the unoccupied states above the Fermi level. The relatively bulk measurements, however, show that $NiCo_2O_4$(001) thin films possess perpendicular magnetic anisotropy (PMA) [3].

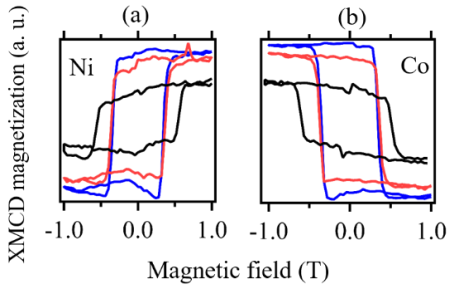

FIG. 5. The magnetic hysteresis, from angle-resolved X-ray magnetic circular dichroism (XMCD) measurements, at the (a) Ni and (b) Co absorption edges of the $NiCo_2O_4$(001) thin film surface at 0^0 (blue hysteresis), 30^0 (red hysteresis), and 60^0 (black hysteresis) angles made by incident circularly polarized x-ray photon with surface normal of the sample.

Considering all angle-resolved XMCD for $NiCo_2O_4$(001) thin film surface, XMCD magnetizations are maximum at around 10^0 (and hence some spin-canting) for both Ni and Co absorption edges. However, for Pt/$NiCo_2O_4$(001) system, XMCD magnetizations at both Ni and Co absorption edges are observed to be maximum at around 30^0 to 40^0 showing significant role of Pt thin layer deposition on $NiCo_2O_4$(001) thin film in spin ordering of $NiCo_2O_4$ at the Pt/$NiCo_2O_4$(001) interface.

References

[1] **A. Subedi**, D. Yang, X. Xu, and P. A. Dowben, J. Phys. D: Appl. Phys., in press, (2024). [https://doi.org/10.1088/1361-6463/ad5aa8]
[2] **A. Subedi**, D. Yang, W. K. Chin, B. Tamang *et al.*, J. Phys.: Condens. Matter **36**, 285001 (2024).
[3] C. Mellinger, J. Waybright, X. Zhang, C. Schmidt *et al.*, Phys. Rev. B **101**, 014413 (2020).