**Front Matter**

**Title**

**Long Title:** Interfacial-Redox-Induced Tuning of Superconductivity in YBa2Cu3O7-δ

**Short Title:** Interfacial Tuning of Superconductivity in YBCO

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**Abstract**

Novel approaches for modifying ion distributions in the solid-state offer unprecedented control over material properties, enabling the development of multifunctional materials. For example, recent works demonstrated control over the Cu-site valence and doping level in cuprate thin films using ionic liquid gating, enabling electrical control over the superconducting transition. We report a scalable approach towards doping level control of superconductivity in films of optimally doped YBa2Cu3O7-δ (YBCO). In our approach, a thin metallic Gd capping layer is sputter deposited onto epitaxial YBCO films. The extremely high oxygen affinity of Gd initiates a solid-state redox reaction at the YBCO interface, removing oxygen from the YBCO. Progressive reduction of the superconducting transition is observed, with complete suppression possible for a sufficiently thick Gd layer. This work demonstrates an effective approach for tuning the superconducting properties of the cuprates and extends the viability of ionic control over the charge doping level to the quasi-bulk regime.

**MAIN TEXT**

**Introduction**

Many of the properties of the high- copper oxide superconductors are strongly influenced by charge doping (*1*, *2*). The ability to control the doping level in these materials is therefore important not only for the development of experimental platforms that enable studies of correlated electron physics, but for multifunctional device applications as well. While traditionally (*3*–*6*) the doping level is fixed during synthesis via chemical substitution or post-growth annealing, recently several techniques have demonstrated approaches which allow for on-demand control. By leveraging electrolytic double layer techniques, gating experiments (*7*, *8*) on RBa2Cu3O7-δ (R=Y, Nd) thin films have achieved control over the Cu-site doping level, which determines the dominant electronic order, by introducing oxygen vacancies into the film under electric fields. In these materials, O2- ions can migrate under the influence of an externally applied electric field to eventually escape through the film surface, resulting in the formation of oxygen vacancies. To maintain charge neutrality electrons are returned to the Cu ions within the film, resulting in a reduction in Cu valence and reducing the hole concentration of the oxide. Signatures of the effects on the electronic order in these materials are profound, and point to the efficacy of oxygen migration and vacancy formation in manipulating the properties of the cuprate superconductors. Recently, we demonstrated a different, solid-state approach to manipulate ionic distributions in oxide thin films by using a reactive Gd capping layer and thus achieved ionic control of magnetism (*9*–*11*). Leveraging the reactivity of Gd, these capping layers can extract oxygen from an adjacent oxide film, with the level of oxygen depletion controlled by the thickness of the Gd and the ion mobility in the oxide, often at room-temperature. Superconducting YBa2Cu3O7-δ (YBCO) is a prototypical example of the high- cuprates, with crystal structure and electronic ordering sensitive to oxygen stoichiometry. Combined with its high ionic conductivity (*12*, *13*), these properties make it an ideal candidate material to explore with this method.

In this study Gd capping layers of varying thicknesses are deposited on 100 nm thick YBa2Cu3O7-δ films, dramatically altering the oxygen distribution throughout the underlying film without any annealing. As the Gd layer thickness () is increased the YBCO layer becomes progressively more oxygen deficient, demonstrating how appropriate tuning of can precisely control the remaining oxygen content of the underlayer. The extraction of oxygen from the YBCO induces a structural transition and alters the superconductivity by reducing and broadening the superconducting transition. Superconductivity is completely extinguished for the sample with thickest capping layer. X-ray absorption spectra (XAS) indicate a reduction of Cu valence state consistent with the removal of oxygen from the YBCO film, particularly from within the CuO chains. Since superconductivity in YBCO relies on charge transfer from the CuO chains to the CuO2 planes, the disappearance of superconductivity may be attributable to the reduction in hole doping level or structural changes, both effects induced by Gd-driven oxygen migration.

**Results**

Commercially available films of pulsed-laser-deposited YBa2Cu3O7-δ (100 nm) grown on (001) SrTiO3 (STO) substrates were purchased for this experiment (*14*). The high-symmetry STO substrate (cubic, Å) is known to yield YBCO films with 90° twinned domains (*15*), with up to 2% tensile strain exerted at the interface due to lattice mismatch (*16*, *17*) (bulk lattice parameters of YBCO are *a* = 3.827 Å, *b* = 3.893 Å, and *c* = 11.699 Å (*18*)). While the strain is known to suppress , the films are expected to relax away from the substrate/film interface (*19*, *20*) and show near bulk-like superconducting behavior (*17*). The films were then sputter coated with Gd layers of varying thickness ( 3 nm, 7 nm, 20 nm) and an Au (5 nm) protective cap, with one witness sample of YBCO/STO kept in the as-grown state for comparison.

X-ray diffraction (XRD) scan of the as-grown film (Fig. 1A) shows only the family of peaks, corresponding to a lattice parameter of *c* =11.678 Å, similar to the bulk value of 11.699 Å (*18*). The slightly smaller *c*-axis lattice parameter may be due to the tensile strain from the substrate (*21*). As is increased, a monotonic shift towards lower is observed in the YBCO diffraction peaks, indicating expansion in the *c*-axis, similar to those previously reported in other perovskite systems (*22*) as a signature of oxygen depletion. Importantly, a second broader feature emerges at lower angles alongside the peaks for nm, indicating the formation of a separate minority structural phase coexistent with the optimally doped majority film. This secondary feature becomes dominant for nm. In addition to the out-of-plane direction, the in-plane structure of the films was probed using reciprocal space maps (RSMs) taken near the STO substrate reflection (Figs. 1B-E, G-J). Coordinates of the RSMs identify the *h* (*x*-axis) and *l* (*y*-axis) Miller indices relative to the STO substrate. When grown on cubic STO substrate, nominally orthorhombic YBCO is expected to form a twinned crystal structure, resulting in a splitting of the in-plane Bragg reflections (*16*). For each sample, the RSM shows a bright substrate peak (Figs. 1B-E), with a lower-intensity, broadened YBCO peak near . Owing to the nearly identical in-plane lattice parameters, two closely spaced Bragg reflections are expected from the and YBCO crystal planes; however, only a single peak is observed in the as-grown YBCO (Fig. 1G). This peak is elongated along , the in-plane direction, suggesting that the and peaks overlap but are too closely spaced to be separately resolved. Thus, before the Gd capping layers are deposited, these films are relaxed in-plane and possess the expected orthorhombic symmetry. As is increased, the YBCO film peak broadens along the (00*l*) direction and shifts to lower , consistent with an expansion in the *c*-axis lattice parameter discussed above.

To examine the effects of Gd deposition on the YBCO superconducting properties, magnetometry and Van der Paw resistivity measurements were carried out between 5 K - 100 K. Zero-field cooled (ZFC) measurements of the sample magnetization (Fig. 2) in a 10 Oe magnetic field show a sharp superconducting transition in the as-grown YBCO film at K, indicating expulsion of the magnetic flux due to the Meissner effect, which is typical of YBCO films grown on STO substrates (*17*). Accompanying the magnetic transition is a precipitous resistivity drop to zero, further confirming the superconducting transition. With increasing Gd capping layer thickness the magnetic transition shows a smooth reduction in the transition temperature , with complete suppression of the Meissner effect for nm. In contrast to the magnetometry, resistivity measurements initially show only a small shift toward lower for nm. However, for nm and nm the superconducting transition is completely suppressed, with no apparent transition down to the lowest measured temperature (5 K).

The differences between the superconducting transitions observed in magnetometry and resistivity can be explained by the presence of a oxygen-deficient (OD) phase with lower Tc, stabilized alongside the optimally doped (OP) YBCO phase. Specifically, for the as-prepared and nm samples, most of the film possesses the initial structure and nominal stoichiometry of YBa2Cu3O7-δ. By comparison, the nm sample shows a transition in the magnetometry, but not in the resistivity. The magnetic signal arises from the Meissner effect and scales directly with the superconducting volume fraction of the film, while the superconducting transition in the resistivity necessitates a contiguous superconducting pathway to exist through the sample. Therefore, the nm sample possesses some fraction which is still superconducting, as evidenced by the magnetometry, but is beyond the percolation limit for the resistive OD phase, as evidenced by the absence of a transition in the resistance. Finally, for the thickest nm sample the absence of a transition in either the resistance or magnetic data suggests few, if any, regions undergo superconducting transition in the sample. The distinctly different superconducting properties of the OD phase may be the result of structural changes or electron doping, both of which are consequences of the oxygen leaching.

The Gd capping layer is expected to extract oxygen from the YBCO, resulting in the structural changes that were observed in XRD patterns. Cross-sectional high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of the as-grown film at the STO/YBCO interface show flat, epitaxial YBCO growth consistent with XRD patterns. The layered structure of YBa2Cu3O7-δ is well resolved, with bright Ba-Y-Ba atoms visible between alternating rows of dark CuO chains and occasional double-CuO layer stacking faults distributed throughout (Fig. 3A-C, inset). In the nm (Fig. 3C and inset) and nm samples, double-CuO stacking faults appear near the surface of the film, while major lattice distortions are visible in the nm film (Fig. 3C). Examples of similar double-CuO stacking faults have been reported in PLD-grown films of YBCO previously (*23*–*25*), where they have been attributed to the limited atomic diffusion range under typical laser deposition conditions. Double- or multi-CuO stacking faults form different microstructural phases than optimally doped YBa2Cu3O7-δ (Y-123, with numbers denoting cation stoichiometry), e.g. Y-124 and Y-247; they directly alter the YBCO doping centers, which in turn affects the superconducting transition, and have lower critical temperatures than Y-123 (*26*–*29*). These stacking faults point to the aggressive nature of the oxygen leaching effect, as the YBCO layers near the Gd interface become increasingly disrupted when oxygen is removed from deep within the film, and suggest that changes to the microstructure likely play a key role in the suppression of superconductivity.

The extraction of oxygen was further probed by polarized neutron reflectometry (PNR), which provides a depth-resolved mapping of the nuclear scattering centers within the film. The converged depth profiles (Fig. 4) confirm the expected thickness of the as-grown structure, while the nuclear scattering length density (SLD, ) of the as-grown film is similar to the calculated value for YBa2Cu3O7 of . With increasing the YBCO layer increases in thickness, in qualitative agreement with the unit cell expansion observed in XRD. Commensurate with the progressive increase in thickness, the nuclear SLD decreases, particularly near the YBCO/Gd interface, consistent with the removal of oxygen from the YBCO. In addition to the standard nuclear profile, the Gd layer is explicitly identifiable by the imaginary component of its SLD, which corresponds with neutron absorption. Since Gd is the only significant neutron absorber present in this system, the imaginary component of the nuclear SLD allows us to rule out the possibility of YBCO/Gd interdiffusion.

While the PNR results are consistent with the extraction of oxygen from the YBCO, fluorescence yield (FY) XAS measurements performed at the Cu *L*2,3-edges directly confirm a change in the Cu valence resultant from the oxygen extraction. The XA results (Fig. 5) show a shift in the absorption resonance to lower energies with increasing . Similar spectral shifts reported in other oxygen-deficient perovskite systems (*30*, *31*) have been attributed to a decrease in the average Cu valence, the result of electrons returning to the Cu ions as oxygen is leached from the film. The shoulder at eV in the as-grown YBCO spectra, a feature characteristic of lower-valence ligand states present in CuO chains (*8*, *32*–*34*), is suppressed for greater , confirming the loss of oxygen within the chains. A second resonance associated with the Cu1+ valence state emerges at eV for 7 nm and 20 nm. This new absorption peak, appearing in conjunction with the emergent low angle feature observed in XRD, again points to the formation of a stable OD phase. The bulk sensitivity of FY measurements (70% X-ray transmission through 100 nm of YBCO at Cu-*L*2 resonance) infers that the observed oxygen depletion comes from ionic migration from deep within the film despite the interfacial origin of the leaching effect. The high ionic conductivity required for such long-range oxygen migration is in agreement with previous reports (*12*, *13*). The known sensitivity of the YBCO superconductivity to the oxygen stoichiometry suggests that this approach may therefore be used as a mechanism to design the superconducting transition.

**Discussion**

In summary, Gd capping layers deposited at room temperature on optimally doped YBCO thin films have been shown to remove oxygen from the underlying film via an interfacial redox reaction, with the extent dependent on capping layer thickness. This redox-induced oxygen migration results in a percolative phase transformation from the optimally doped state to an oxygen deficient state which does not support superconductivity. As measured in magnetometry and resistivity, the superconducting transition temperature is significantly reduced with increasing Gd thickness, and for sufficiently thick capping layer, the transition is extinguished completely. X-ray spectroscopy measurements indicate that the CuO planes become progressively more oxygen deficient with increasing Gd thickness, while the average Cu valence decreases. The emergence of a separate peak in XRD confirms the formation of a new structural phase, suggesting that both changes to the microstructure as well as a reduction in hole doping level may play roles in the suppression of superconductivity. Remarkably, the changes to the superconducting properties throughout the entire 100 nm thick YBCO films are induced by the migration of oxygen towards the YBCO/Gd interface, extending the viability of this approach for controlling the hole-doping level to the quasi-bulk regime.

**Materials and Methods**

**Film growth and characterization**

Commercially available 100 nm thick YBCO films grown on STO substrates were purchased and subsequently sputter coated with Gd (3 nm, 7 nm, 20 nm) and a Au (5 nm) protective capping layer using Ar gas at Pa working pressure in a chamber with a base pressure of Pa. XRD characterization, including both symmetric scans and reciprocal space maps, was performed on a X-ray diffractometer equipped with parallel beam optics and Cu monochromator. Polarized neutron reflectometry was measured at the NIST Center for Neutron Research on the PBR and MAGIK beamlines. The experiment used 5 Å neutrons, and were carried out at a temperature of 6 K. Fitting of the PNR data was performed using the Refl1d software package, following a Markov-chain Monte Carlo fitting algorithm(*35*). The calculated SLD was determined by the calculating the sum of the volume-scaled atomic scattering lengths. XA measurements were performed at the Advanced Light Source on beamline 4.0.2 at room temperature in a grazing incidence (30°) geometry. Both fluorescence and electron yield (EY) modes were measured, but due to the capping layers no appreciable signal was measured in the EY mode. Magnetometry measurements were performed in a field of 1 mT. To reduce stray magnetic fields, the magnet was purged before each measurement. Resistivity was measured using a four-contact Van der Pauw geometry. The current used was 100 µA at frequency of 173 Hz. The magnetic field at the sample was set to zero before the measurement by setting the temperature to the midpoint of the superconducting transition before adjusting the applied field to minimize the resistivity.

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**Author contributions:** P.D.M., D.A.G. and K.L. coordinated the project. P.D.M. synthesized the samples, carried out structural analysis, and prepared the first draft of the manuscript. D.A.G., A.J.G., B.J.K, and J.B. performed PNR studies. D.A.G. and A.J.G. and E. A. carried out XAS measurements. D. H-M. and M.V. performed electron microscopy studies. V. T. measured magnetometry. Z.E.B., J.R.J., and R. Z. carried out transport measurements. R.V.C. and Y.T. assisted with sample synthesis and RSM studies. All authors contributed to data analysis and manuscript revision. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** Experimental data is available upon request.

**Figures**

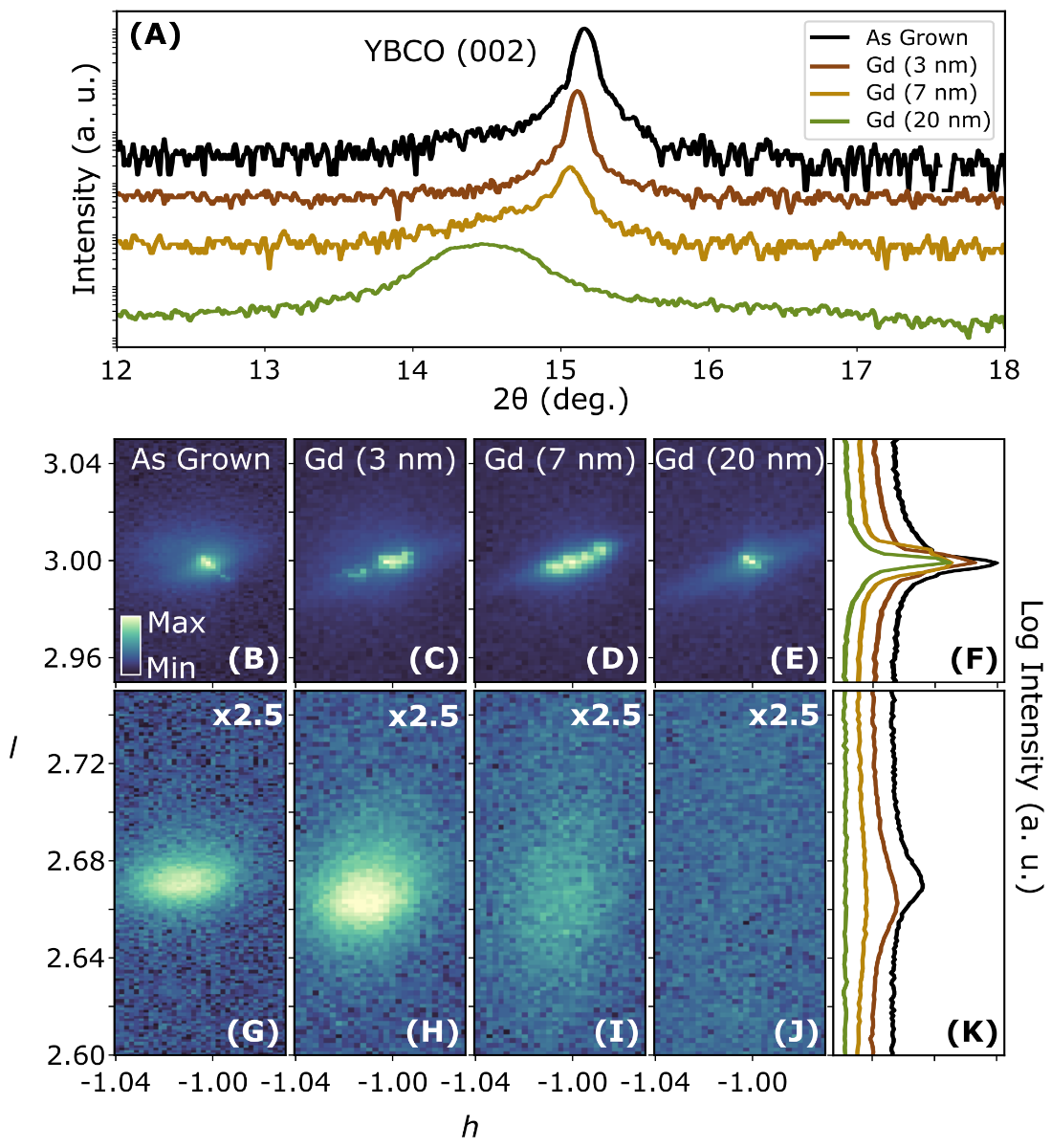
**Fig 1**. **X-ray diffraction.** (**A**) XRD scan near the (002) YBCO peak measured with Cu radiation. Reciprocal space maps showing (**B-E**) the () STO substrate peak, (**G-J**) ()/ () YBCO peak, and (**F, K**) projections of each map along the -direction.

**Figure 2**. **Magnetization and resistivity.** Normalized magnetization (**A**) and resistivity (**B**) from 5 K to 100 K. The Gd (20 nm) sample has been omitted from (**B**), as no magnetic moment was detected at any temperature measured (to within experimental noise).

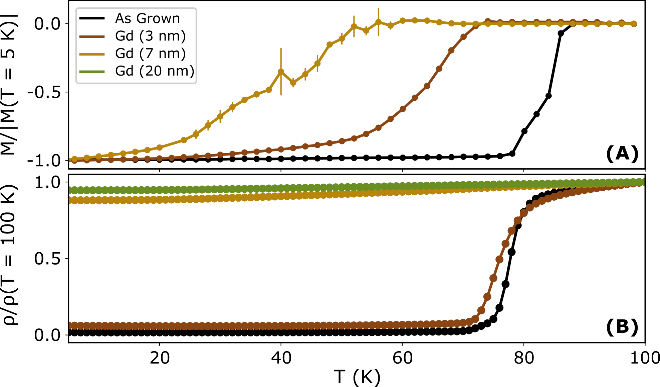
**Figure 3**. **STEM images.** Cross-sectional HAADF-STEM images of the as-grown STO/YBCO interface (**A**), the YBCO/Gd interface of the Gd (3 nm) (**B**) sample, and center of the YBCO layer in the Gd (20 nm) film (**C**). Red arrows in (**B**) show examples of double- or poly-CuO stacking faults. The inset shows the region highlighted by the black box, with a stacking fault visible running down the center. The crystal structure is also depicted, with Cu, Ba, and Y atoms highlighted in yellow, red, and blue, respectively.

**Figure 4**. **Polarized Neutron Reflectometry.** Real (**A**) and imaginary (**B**) part of the nuclear SLDs as a function of depth through the sample as measured by PNR. Grey region () corresponds to the substrate, with the approximate location of the YBCO, Gd, and Au layers given by the shaded regions for ().

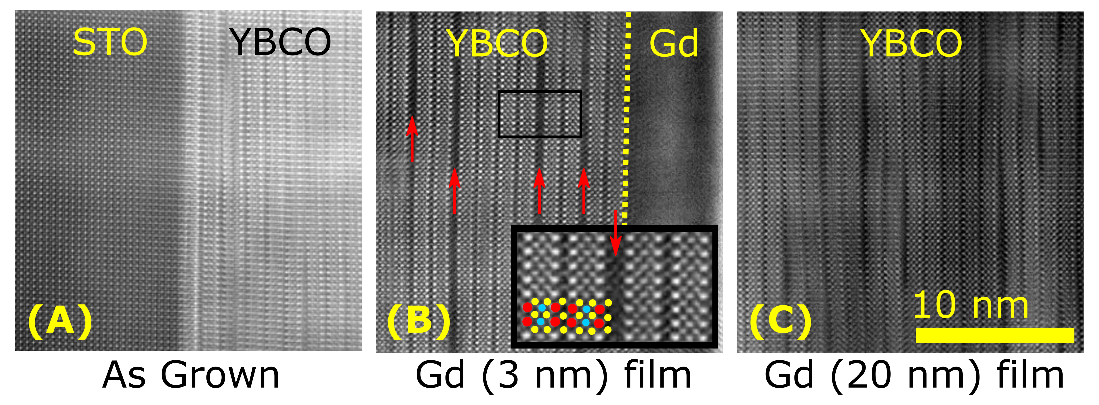
**Figure 5**. **X-ray Absorption Spectra.** Close-up view of the normalized absorption spectra as a function of incident X-ray photon energy near the Cu *L3*-edge, as measured in fluorescence yield mode. The full spectral range measured including the Cu *L2*-edge is shown in the inset, with the shaded region corresponding to the close-up view.



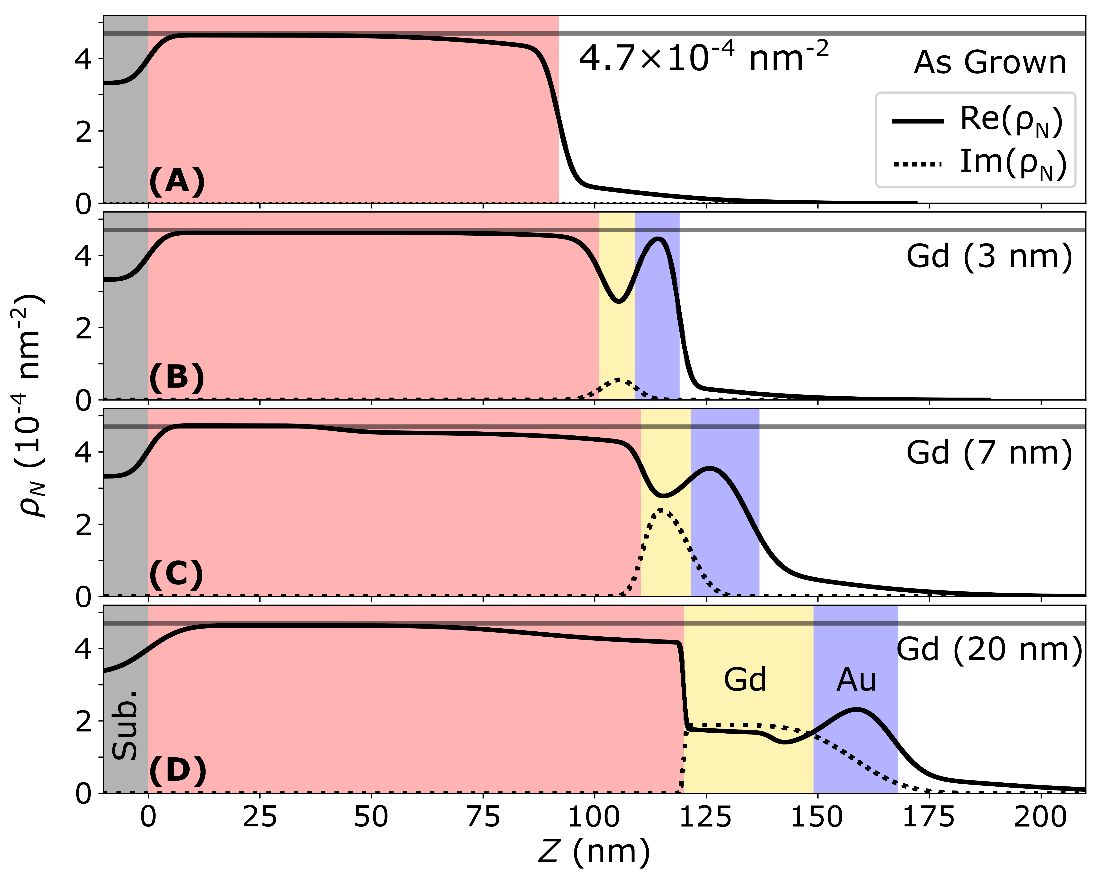
**Fig. 1**



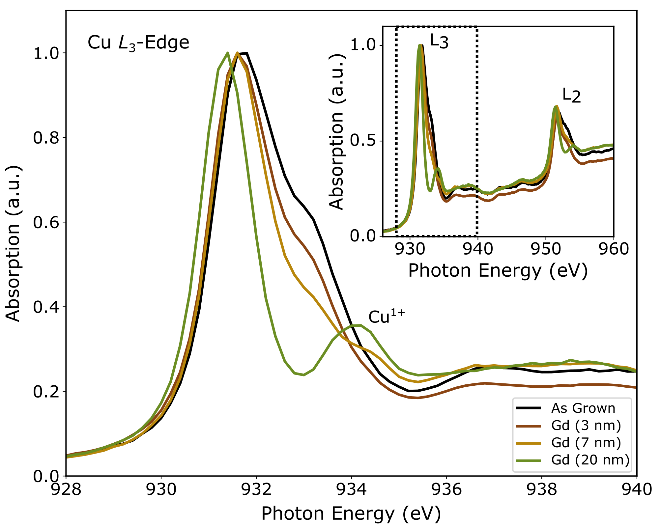
**Fig. 2**



**Fig. 3**



**Fig. 4**



**Fig. 5**