

X-ray and electron nondestructive spectroscopic methods for thin films and interfaces study. Application to SrTiO₃ based heterostructures

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We are focusing on the developed by us the mathematical analysis methods of the data obtained by three independent spectroscopic techniques and their application to study of atomic and chemical composition profiles across the air-exposed systems SrTiO_x/B/Si with interfacial layers (B: SiO₂, Si₃N₄ and HfO₂) grown by the atomic layer deposition technique. It was established that the material of the interlayer influences strongly the crystallinity of the SrTiO₃ film. Only the Si₃N₄ interlayer supports the Sr surface enrichment of the film in atmosphere. The HfO₂ interlayer promotes the violation of the crystalline structure creating numerous defects. The SrCO₃ content depends strongly on the crystallinity of the film.

The renewal of interest to the well-known SrTiO₃ is caused both by its good electrical characteristics ($k \sim 150-300$) and also by advances in the atomic layer deposition method of synthesis, which provides the aggressive conformality of SrTiO₃ thin films at a reasonably low processing temperature required for DRAM capacities. A special role in the formation of the film belongs to the interface of the dielectric film with silicon. SrTiO₃ is thermodynamically unstable in direct contact with Si that leads to the formation of titanium silicide and alkaline-earth silicate. In order to improve the dielectric properties of SrTiO₃ thin films, a thin interlayer is introduced between the substrate and SrTiO₃ film. An additional way to a substantial change in the electrical properties of SrTiO₃ is the violation of the stoichiometry of SrTiO₃. The main goal of this work is to study the influence of the material of interlayer between film and substrate on the crystallization behavior and microstructure of the Sr-rich SrTiO₃ films using different nondestructive spectroscopic methods. A special attention will be drawn to the possibilities of three non-destructive spectroscopic techniques (Hard X-Ray Photoelectron Spectroscopy (HAXPES), depth resolved soft x-ray emission spectroscopy (DRSXES) and Soft X-Ray Reflectometry (SXRR)) to study of atomic and chemical composition profiles across the heterostructure with in-depth resolution better than 1 nm.

HAXPES is a very effective non-destructive depth sensitivity technique for chemical analysis of nano-layered systems, which can be realized by changing the photoelectron's emission angle or/and kinetic

energy of photoelectrons [1]. DRSXES uses energy dependence of the primary electron penetration depth to determine atomic composition from the characteristic X-ray emission lines with in-depth resolution [2, 3]. The reflectivity curves measured as a function of the incident angle and at different soft-x-ray photon energies make possible the determination of depth-distribution of all chemical elements (atomic concentration profiles) composing a sample [4].

As an example fig.1 shows the experimental and fitted Sr 3d photoelectron spectra from thick (15 nm) films after normalization. The joint analysis of all the photoelectron and NEXAFS spectra reveals the following regularities: 1) the SrCO₃ content depends strongly on the crystallinity of the film; 2) considering that larger excitation energy corresponds to an increased probing depth, we conclude that a SrCO₃ structure has formed predominantly at the surface of all the samples; 3) only the film grown on SiO₂ interlayer corresponds to the stoichiometric SrTiO₃; two other films show a violation of the structure; 4) only the Si₃N₄ interlayer supports the Sr surface enrichment of the film in atmosphere. The HfO₂ interlayer promotes the violation of the crystalline structure creating numerous defects; 5) for the studied film thicknesses thin films differ only slightly from thick films.

Reconstruction of the atomic concentration profiles from the measured reflectivity curves was performed for all the studied samples in framework of the simplest three-layer model [1,4]. The thickness and the density of all three layers are considered as fitting parameters, while the density of the Si substrate is supposed to be known. There are four interfaces in this model, and their widths are considered as fitting parameters. The stoichiometry of Sr-containing layer was assumed to be SrTi_xO_y, where x and y are unknown, so that the total number of the fitting parameters was 12. As an example the reconstructed atomic concentration profiles for SrTiO₃(15nm)/SiO₂/Si and SrTiO₃(7nm)/Si₃N₄/Si samples are shown in the fig.2. It was established: 1) the internal structure of the samples with the same interlayer is almost independent on the studied thickness films and is quite different for the samples with different types of interlayer; 2) only the Si₃N₄ interlayer supports the enrichment of the film in atmosphere. Presumably the enrichment of Sr occurs

predominantly in the near surface range of the film; 3) the interface width between Si-substrate and interlayer is rather wide for the samples on SiO₂ and HfO₂; for the samples on Si₃N₄ interlayer the interface is very abrupt; 4) surface of the samples prepared on SiO₂ and Si₃N₄ is very smooth (is close to the Si substrate rms roughness), while it is rougher for the samples prepared on HfO₂ interlayer.

References

- [1] E. O. Filatova et al, Sci. Technol. Adv. Mater. 13 (2012) 015001-015013
- [2] A.S. Shulakov, Cryst. Res. Technol. 23 (1988) 835-838.
- [3] A.V. Zimina et al, Surf. Rev. Lett. 9 (2002) 461-467.
- [4] E. O. Filatova et al, Ch.7 in "High-k Gate Dielectrics for CMOS Technology", Gang He and Zhaoqi Sun, Eds., Wiley-VCH Verlag. Weinheim, Germany, 2012, pp.225-271

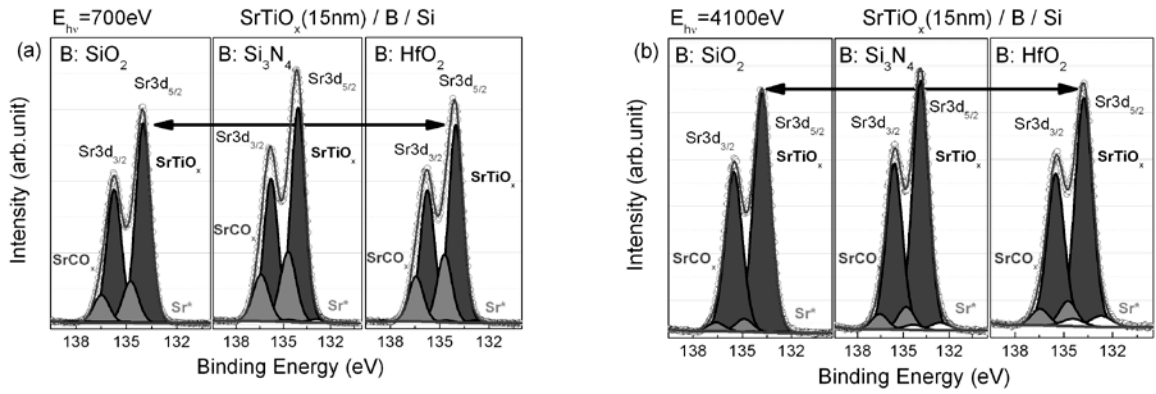


Fig.1: Experimental and fitted Sr 3d photoelectron spectra from SrTiO_x(15nm)/B/Si samples measured: (a) at an excitation energy of 700 eV and normal emission angle after cleaning and (b) at an excitation energy of 4100 eV and 10° emission angle.

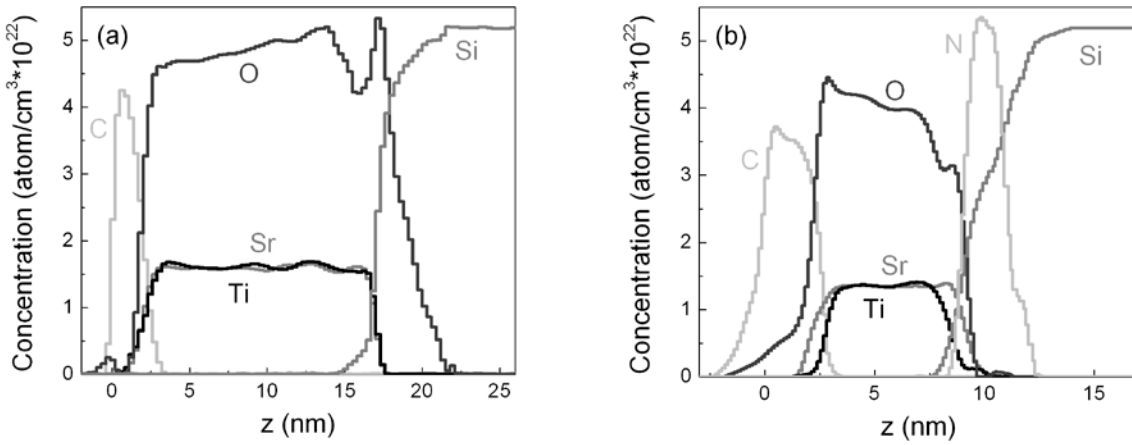


Fig.2: Derived depth-distributions of atomic concentrations for the samples SrTiO₃ (15nm)/SiO₂/Si (a) and SrTiO₃(7nm)/Si₃N₄/Si (b).