ELECTRICAL PROPERTIES OF AN AMORPHOUS ZIRCONIUM OXIDE THIN FILM AND STRUCTURE FORMATION DURING CRYSTALLIZATION

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Key Words: extreme non-stoichiometry, thin film, high conductivity, amorphous, zirconium monoxide

Metastable amorphous oxides with a strong oxygen deficiency often show surprising phenomena upon relaxation into thermodynamically stable phases. For example, Nagarajan et al. found a new type of chemically driven insulator-metal transition in highly non-stoichiometric gallium oxide films (GaO_x).[1] Here, an internal solid-state disproportionation reaction leads to the growth Ga_2O_3 nuclei in the initially insulating GaO_x matrix which thereby attains metal-like conductivity. Moreover, it has been recently shown that such films can act as memristive switches. [2]. Highly non-stoichiometric titania (TiO_1.6) films show a similar disproportionation reaction upon heating but as the phase diagram for this material is more complex, various phases can be found during the relaxation [3].

Here, we apply this approach on highly oxygen deficient zirconium oxide thin films prepared by Pulsed Laser Deposition (PLD). In the O–Zr phase diagram three crystalline modifications, namely the monoclinic, the tetragonal and the cubic phase are reported. All of them show small phase widths and – most importantly – no low valent oxides like ZrO_2 or ZrO are noted. Thin films of amorphous and nonstoichiometric zirconium oxide ZrO_x have been prepared by ablating zirconium metal in non-oxidizing atmosphere (p= 0.2 Pa Ar) at room temperature. The films have been characterized by a variety of techniques like XRD, XPS and conductivity measurements as a function of temperature. The untreated films are black, x-ray amorphous and show dc conductivities of about 30 S/cm which increase during heating, and reach a seven times higher value (200 S/cm). The quenched high conductivity state shows a semiconducting behavior (fig.1). XPS and RBS reveal a 1:1 composition of zirconium and oxygen, i.e. approximately ZrO. The evolution of the structure (XRD) during heating exhibits the monoclinic structure and, furthermore, the tetragonal phase, which appears at temperatures below 500 °C – contrary to the phase diagram. Additionally, it could be shown by in situ TEM analysis that the films consist of a mixture of an amorphous matrix and crystalline regions: At elevated temperatures the tetragonal and monoclinic zirconium dioxide structures were found whereas a cubic phase was detected at low temperatures. The latter matches the pattern of to a cubic zirconium monoxide phase which has been so far only predicted theoretically [4].

Figure 1: DC-conductivity change during heating of a ZrO_x thin film.