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Controlling In–Ga–Zn–O thin films transport properties through density changes

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ABSTRACT

In the following study we investigate the effect of the magnetron cathode current (I_c) during reactive sputtering of In–Ga–Zn–O (a-IGZO) on thin-films nanostructure and transport properties. All fabricated films are amorphous, according to X-ray diffraction measurements. However, High Resolution Transmission Electron Microscopy revealed the a-IGZO fabricated at $I_C = 70$ mA to contain randomly-oriented nanocrystals dispersed in amorphous matrix, which disappear in films deposited at higher cathode current. These nanocrystals have the same composition as the amorphous matrix. One can observe that, while I_C is increased from 70 to 150 mA, the carrier mobility improves from $\mu_{Hall} = 6.9$ cm^2/Vs to $\mu_{Hall} = 9.1$ cm^2/Vs. Additionally, the increase of I_C caused a reduction of the depletion region trap states density of the Ru–Si–O/In–Ga–Zn–O Schottky barrier. This enhancement in transport properties is attributed to the greater overlapping of s-orbitals of the film-forming cations caused by increased density, evidenced by X-ray reflectivity, at a fixed chemical composition, regardless nanostructure of thin films.

1. Introduction

Transparent amorphous oxide semiconductors (TAOSs) such as In–Ga–Zn–O (a-IGZO) are a subject of intensive theoretical and experimental research aimed at applications in thin-film transistors (TFTs), as an enabling technology for novel displays, communication, computing, and identification devices [1,2]. This is owing to the fact that a-IGZO combines X-ray amorphous microstructure with electron mobility above $\mu > 10$ cm^2/Vs, even when fabricated at room temperature. This arises from the nature of the chemical bonding in TAOSs, whose conduction band minima are composed of spherical isotropic s-orbitals of the metallic cations. Owing to the spherical symmetry of s-orbital the neighboring orbitals always overlap, if the radii of these orbitals are larger than inter-cation distances, despite the degree of disorder in the material. This means that even in the amorphous state, TAOSs could have a well-defined carrier path in the conduction band minimum and large mobility may be achieved [3]. These properties alongside the high optical transparency make a-IGZO one of the most promising materials for transparent TFTs and circuits, flexible devices and system-on-plastic applications [4]. To date many researchers have improved characteristics of a-IGZO TFTs and consequently demonstrated a field-effect mobility above 10 cm^2/Vs, a subthreshold swing down to 0.06 V/dec, and an on–off current ratio greater than 10^{10} [5]. Nevertheless, in order to further improve quality of such devices, fundamental research focused on understanding the a-IGZO structure–property-processing relationships is still needed. It is acknowledged that total deposition pressure and oxygen partial pressure during sputtering processes significantly alter a-IGZO properties [6–8]. Additionally, it was also reported that impurity hydrogen may affect a-IGZO TFT parameters [9]. Moreover, Ide et al. show that weakly-bonded oxygen is an important factor influencing a-IGZO properties as well [10]. In the following study, we have focused on effects of $InGaZnO_4$ magnetron cathode current (I_C) during radio frequency (RF) sputter-deposition of thin films on their properties, since there are notable differences in carrier concentration and mobility of a-IGZO deposited under different I_C, and no previous systematic study was published in this field. Since TAOSs other than their crystalline counterparts, cannot be correctly described by looking at their structure, it has been difficult to optimize such materials with reference to the classical structure–property correlation paradigm. Thus, tools that could complement the X-ray diffraction (XRD) results are required for studies of the a-IGZO properties. Therefore, we performed High Resolution Transmission Electron Microscopy (HRTEM) and Atom Probe Tomography (APT), the only method today that offers three-dimensional analysis of materials on an atomic scale [11] and thereby provides crucial physicochemical information

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necessary to understand the connection between the fabrication process and properties of a-IGZO. APT relies on a successive removal of single surface atoms from a very sharp (<100 nm radius) needle-shaped sample by using either very short high voltage or laser pulses. During this process atoms on the tip surface are torn off by field evaporation and become ionized. The removed ions arrive subsequently at a position-sensitive detector where their impact coordinates are recorded, thereby making reconstruction of the positions of the ions in the sample possible. The identity of the ions is determined by time-of-flight mass spectrometry. Consequently, the atomic-scale chemistry of the sample volume is reconstructed with nearly atomic resolution and with equal sensitivity for all elements [11].

2. Experimental details

100 nm thick a-IGZO films were fabricated on quartz substrates by RF reactive magnetron sputter-deposition from a stoichiometric $InGaZnO_4$ ceramic target in Ar/O_2 plasma without intentional heating. During sputtering total deposition pressure and oxygen content in the plasma were kept constant at 0.6 Pa and 0.5%, respectively. During the deposition I_C was equal to 70, 110 and 150 mA. Target-to-substrate distance was equal to 35 mm. Carrier concentration and mobility of a-IGZO films were determined by Hall-effect measurements in van der Pauw configuration. Microstructure was analyzed by means of XRD and HRTEM. The density of thin films was evaluated from X-ray Reflectometry (XRR). The samples for HRTEM were deposited on microscope carbon grids. For APT measurements 100 nm thick a-IGZO films were deposited with the same processes on substrates containing pre-fabricated silicon posts. The preparation of needle-shape specimens for APT analysis was performed by using a FEI Versa 3D DualBeam focused ion beam workstation, equipped with a scanning electron microscope (FIB-SEM) [12]. In order to reduce the implantation of $^{69}Ga^+$ ions and sample degradation, a protecting 1 μm thick platinum layer was deposited before milling. As a second step, the posts located along the axis of the ion beam were subjected to an annular milling. This was carried out with a $^{69}Ga^+$ ion beam at 30 kV using gradually decreasing currents ranging from 240 pA to 6.9 pA, followed by polishing steps at 5 kV using a 22 pA current. By reducing the diameter of the milled circles, the posts were thinned to a sharp tip with a curvature radius smaller than 70 nm. The APT measurements were carried out using a laser-assisted local electrode atom probe LEAP Imago LEAP 3000X HR. In order to compare composition and short range ordering between different APT measurements, they were performed at 30 K by laser pulsing with a wavelength of 532 nm at the frequency of 200 kHz with 200 pJ pulses. Reconstructions of the APT data were created by using the CAMECA IVAS 3.6.6 software.

3. Results and discussion

Deposition rate and transport properties of a-IGZO films fabricated at I_C from 70 to 150 mA are depicted in Fig. 1a and b, respectively. They reveal that the deposition rate increases from 0.09 nm/s to 0.8 nm/s with I_C due to increased sputtering yield at higher current. dditionally, the free carrier mobility (μ_{Hall}) and concentration (n) increase as a function of I_C from $\mu_{Hall} = 6.9$ cm^2/Vs and $n = 9.7 \times 10^{15}$ cm^{-3} to $\mu_{Hall} = 9.1$ cm^2/Vs and $n = 3.7 \times 10^{17}$ cm^{-3}. These results will be explained further in the text when correlated with density measurements. Fig. 2a shows the XRD measurement results of fabricated a-IGZO films. Wide-angle XRD patterns for all samples show only one broad peak at $2\Theta = 22°$ corresponding to the quartz substrate, implying that all films have an amorphous or nanocrystalline microstructure.

In order to probe the structure of a-IGZO films in greater detail, transmission electron microscopy was performed. The bright-field HRTEM images, shown in Fig. 2b–d, demonstrate that a-IGZO deposited at $I_C = 70$ mA contains randomly-oriented nanocrystalline inclusions with diameters in the range of 3–5 nm, while films fabricated at $I_C =$ 110 and 150 mA are amorphous. Selected-area electron diffraction (SAED) patterns acquired with an electron probe of 5 nm size confirm this observation. The SAED obtained from a-IGZO deposited at $I_C =$ 70 mA reveals a mixed microstructure of amorphous and crystalline phases. As $InGaZnO_4$ magnetron cathode current increases, the microstructure tends to be fully amorphous. The rings present in the SAED patterns are related to carbon grid, the sample deposited at 70 mA is the only one having visible spots in the image relating to diffraction of electrons on the nanocrystals in the film. Despite the nanocrystalline inclusions being present, which could serve as scattering centers in a-IGZO fabricated at $I_C = 70$ mA, it was reported that grain boundary-related issues are not the main factors controlling the transport properties of TAOSs. This agrees with similar changes, which we observe for the transport properties in films deposited at higher I_C, and thus without nanocrystalline inclusions. Additionally, Kamiya et al. reported that, owing to percolation and trap-limited conduction mechanisms, the carrier mobility–concentration relationship remains the same even for single-crystalline IGZO, and is therefore not deteriorated by the degree of microstructural disorder [2,13]. Consequently, even though there are no clear grain boundaries in a-IGZO films deposited at $I_C = 110$ and 150 mA, an increase in mobility with an increase in

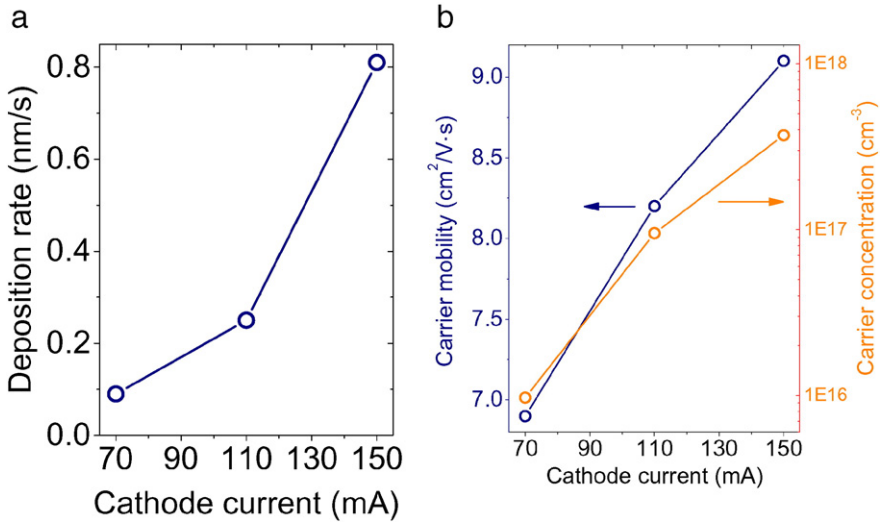

Fig. 1. Deposition rate (a) and transport properties of a-IGZO thin films as function of $InGaZnO_4$ magnetron cathode current.