Investigation of nanostructured glass-ceramic MOS devices

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INTRODUCTION

In this work we present the results of a preliminary structural and functional characterization of a novel glass-ceramic thin film material, in the perspective of applications in UV-C sensing and memristance devices. The investigated system constitutes the first example of glass-ceramic candidate for such technological areas, with not negligible advantages, especially in hazardous environments. The present results demonstrate the feasibility of fabrication of nanostructured oxide-in-oxide thin films with unconventional charge transport mechanisms, suitable to enable the design of memristive devices.

MATERIAL DESCRIPTION

The investigated material is a mixed oxide with molar composition $7.5Li_2O - 2.5Na_2O - 20Ga_2O_3 - 25GeO_2 - 45SiO_2$. Bulk form has been obtained by melt quenching technique, whereas Thin Film (TF, about 50-100 nm thick) have been produced by RF-sputtering from a bulk target on a p-doped silicon substrate. We have previously studied the bulk version of the investigated material, discovering the occurrence of thermally activated phase segregation, nucleation and nano-crystallization [1], then proving the efficient interaction with UV-C light and the resulting properties of solar-blind UV-to-visible conversion [2]. In the case of films, no data is available in the literature either on an analogous nanostructuring or on the photophysical response. To fill this gap, in this work we have investigated the material As Is (or As Deposited for the thin film, AD) and after a Thermal Treatment (TT) consisting in an annealing at 670°C for 30 minutes. This temperature has been chosen according to DSC measurements on the bulk [1] that shows a phase transition in this region related to the formation of γ-Ga_2O_3 nanoparticles (NPs).

METHODS

Both TF and bulk, before and after TT, have been investigated via X-Ray Diffraction (XRD) and Electron Microscopy (EM) imaging. On the thin films we have also performed Atomic Force Microscopy (AFM) analysis and a detailed electrical characterization after deposition of a top metal electrode of 50 nm of chromium. The characterization has been carried out by means of an LCR meter operating in the frequency range between 100 Hz and 1 MHz with and without an applied DC bias.

MORPHOLOGY

The XRD spectra (figure 1) show a very broad unstructured band in every samples, as expected from the amorphous component of matrix, mainly composed by a silicate glass. in the spectra collected on TT bulk samples, there is also the presence of peaks ascribable to the γ phase of gallium oxide. Shoulders in the same regions can be also detected in AI bulk samples and TF samples, suggesting the presence of phases of poor crystalline quality.

EM analysis were helpful in the understanding phase separation of these glassceramics. Transmission and scanning EM images (figure 2) highlights different electronic densities between nanophase and matrix, with the latter showing a less pronounced electron density, in accordance with the formation of semiconductive Ga_2O_3 nanoparticles. More interestingly, nanopartcile formation can be observed in TF samples even without the need of any thermal treatment. AFM images (figure 3) on TF samples allowed us to estimate NPs size (diameter from 100 to 300 nm) and their surface density (about 10^{10} NPs/cm^2).

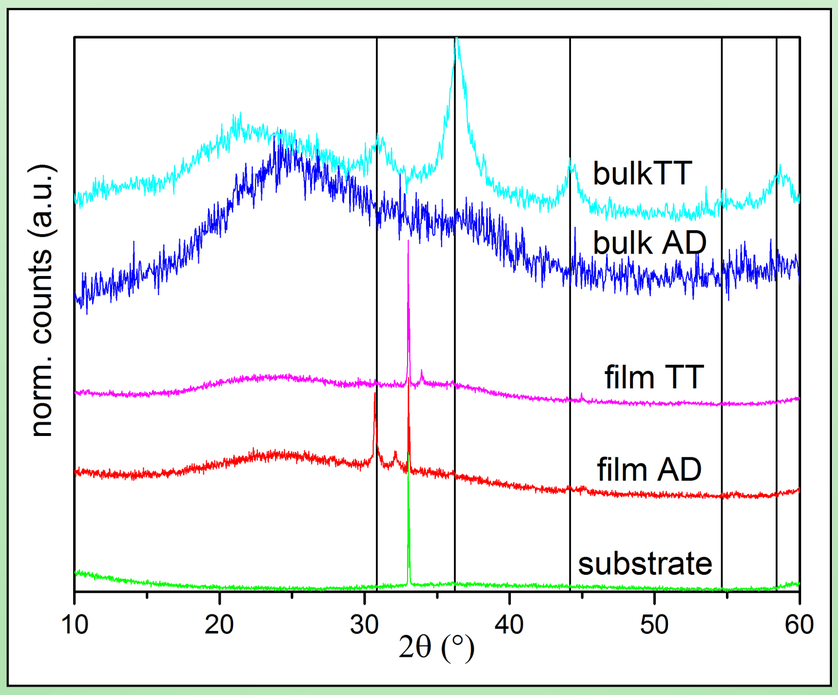

Figure 1: XRD spectra of samples and the film substrate (spectra are upshifted for clarity) with expected peak positions of γ-Ga_2O_3 (vertical grey lines).

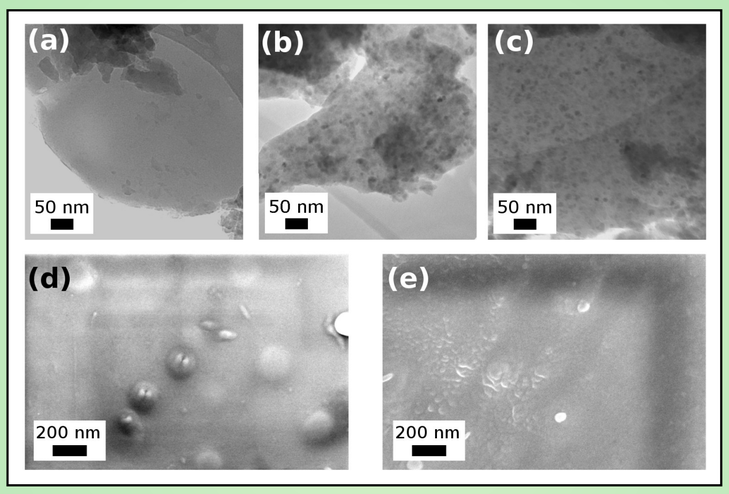

Figure 2: Transmission EM images collected on the bulk before (a) and after 25 (b) and 90 (c) hours of thermal treatment and scanning EM images on the TF before (d) and after (e) 30 minutes of thermal treatment. Nanostructures are absent only in (a).

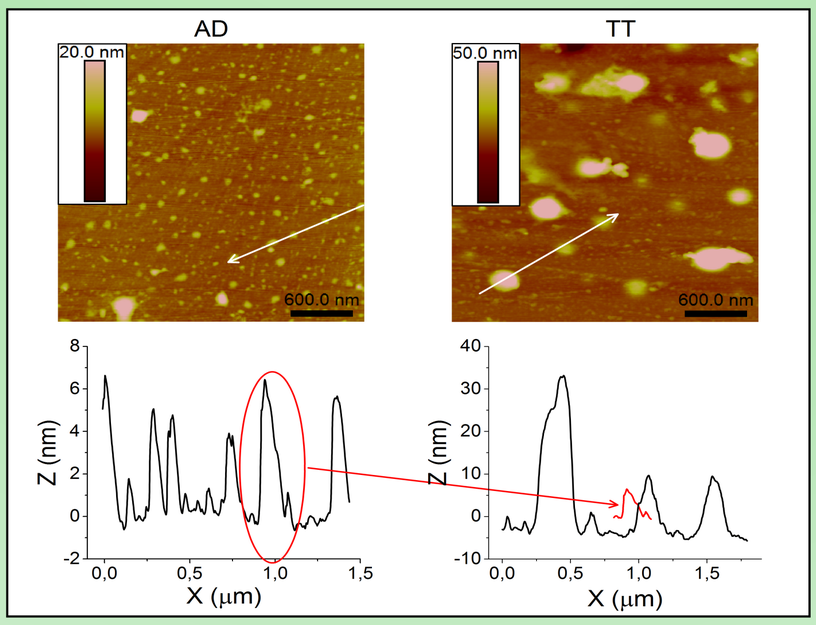

Figure 3: AFM maps (top) and profiles (bottom) of films before (left) and after (right) thermal treatment.

ELECTRICAL RESULTS

Comparison (figure 4) of electrical measurements acquired on our sample and a standard [3] shows a behaviour different from the expected p-like MOS response, but compatible with our glassceramic film acting as a n-semiconductor. Where charge carriers are probably due to the presence of oxygen vacancies and/or germanium and silicon impurities in the Ga_2O_3 nanostructures. The resistivity varies on a wider range than SiO_2-made devices, whereas dielectric permittivity is lower. Such a low value is physically unacceptable, and probably we have to consider capacitor geometry is other than a simple sandwich configuration.

Conductivity collected at different temperatures (figure 5) linearly increases with temperature and energy barriers are not involved in the main process.

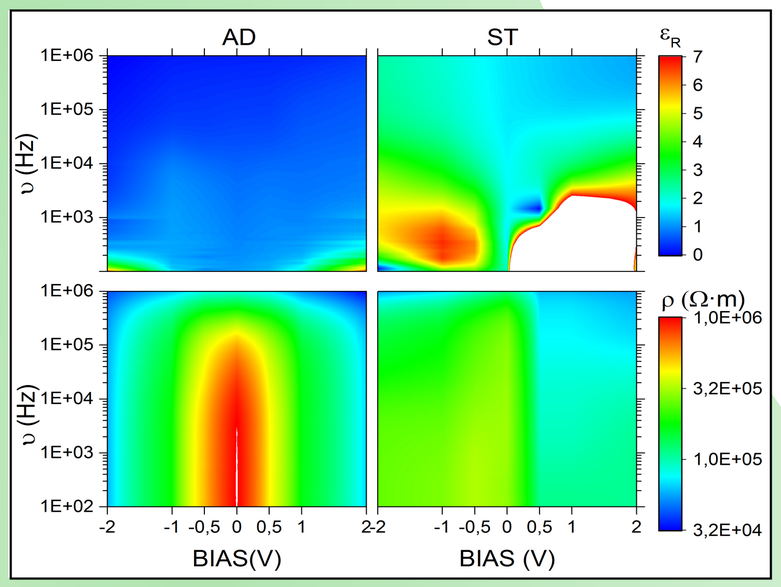

Figure 4: maps showing the resistivity (bottom) and the relative dielectrical permittivity (top) of our AD sample (left) compared to a standard [3] (right). White areas correspond to values greater than the maximum of the color scale.

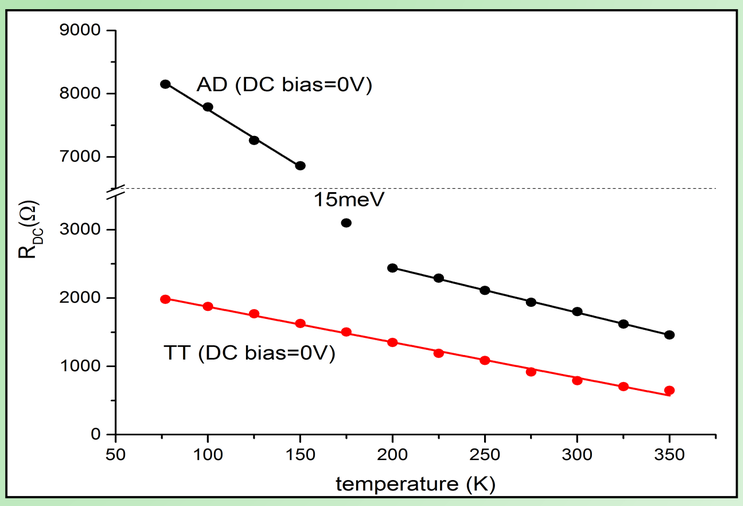

Figure 5: low frequency electric resistance acquired without any DC bias as a function of temperature on TT (red empty points) and AD (black filled points) samples. Both data series show a linear decrease of resistance; the AD sample also show a discontinuity at a thermal energy of about 15 meV, compatible with donor levels in the bulk sample [2].

CONCLUSION

The evidences here reported suggest that the kinetic mechanism that leads to the formation of nanocrystals in thin films does not require any thermal energy, as in the bulk form, but the deposition process, characterized by a slow growth rate (about 240 nm/h) allows the atoms to relocate to their thermodynamic minima, that corresponds to an amorphous matrix with embedded crystalline nanostructures. A subsequent thermal treatment give this nanoparticles the sufficient energy to coalesce in bigger structures. This process also suggests that bigger nanoparticles are thermodynamically favored, but kinetically unfavored at room temperature.

REFERENCES

[1] V. N. Sigaev et Al.; Native amorphous nanoheterogeneity in gallium germanosilicates as a tool for driving Ga2O3 nanocrystal formation in glass for optical devices. Nanoscale, 2013, 5, 299.

[2] V. N. Sigaev et Al.; Light-emitting Ga-oxide nanocrystals in glass: a new paradigm for low-cost and robust UV-to-visible solar-blind converters and UV emitters. Nanoscale, 2014, 6, 1763

[3] MOS from STMicroelectronics based on PECVD silica and p-doped silicon with oxide thickness similar to our device.