

# Influence of plasma treatments and SnO<sub>2</sub> alloying on the conductive properties of epitaxial Ga<sub>2</sub>O<sub>3</sub> films deposited on C-sapphire by chemical vapor deposition

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**Abstract**—Ga<sub>2</sub>O<sub>3</sub> thin films alloyed with SnO<sub>2</sub>, ranging from 0 to 15 at% Sn in composition, were grown by hot wire CVD on c-oriented sapphire. No conductivity is measured on the samples before or after annealing at 1000°C, while UV transparency is the highest. This result contradicts the effect of Sn<sup>4+</sup> doping observed on materials obtained by other methods. Besides, X-ray diffraction patterns show the epitaxial stabilization of a new phase. The films treated by radio-frequency plasma (hydrogen and argon) show a decrease in transparency and an increase in conductivity. The conductivity also depends on SnO<sub>2</sub> concentration. The hydrogen doping levels as well as polarons (due to oxygen non-stoichiometry) are suspected to play a role on the conductivity mechanism.

**Keywords**—transparent conductor; Ga<sub>2</sub>O<sub>3</sub> alloy; plasma treatment

Ga<sub>2</sub>O<sub>3</sub> presents a gap of 4.9 eV [1]. Its conductivity can be modified by introduction of divalent/tetravalent ions [2]. Then, it presents widest band gap of oxide semiconductor and it is evaluated for ultra-violet optoelectronic [3], high breakdown voltage and low-frequency transistors [4]. Nevertheless, undoped β-Ga<sub>2</sub>O<sub>3</sub> is a dielectric and our study on films grown by chemical vapor deposition shows no conductivity. SnO<sub>2</sub> doping and alloying, as well as plasma treatment, supposed to be able to modify the oxygen non stoichiometry or the hydrogen doping are investigated to clarify the conductivity mechanisms. Hydrogen plasma is chosen as protons are more effective on conductivity than oxygen defects, which are too deep in the band gap to participate to conduction [5].

The films, with a thickness of about 150 nm, were grown by hot wire CVD under a 10 Torr pressure on a c-oriented sapphire substrate heated at 700°C. Ga<sub>2</sub>O<sub>3</sub> films are epitaxially grown, as confirmed by XRD and pole figure. The effect of SnO<sub>2</sub> alloying from 0 to 15 at.% is shown on the X-ray diffraction patterns recorded in  $\theta/2\theta$  configuration. β-Ga<sub>2</sub>O<sub>3</sub> exhibits a preferential growth direction according to the (-201) plans, but the incorporation of SnO<sub>2</sub> shows the extinction of some reflections, revealing the presence of a c glide plane. This results indicate that SnO<sub>2</sub> (15 at.% Sn)-Ga<sub>2</sub>O<sub>3</sub> crystallize with the space group C2/c where as β-Ga<sub>2</sub>O<sub>3</sub> adopts the C2/m space group. No impurity phases are observed. Transmission electron microscopy on β-Ga<sub>2</sub>O<sub>3</sub> shows nanocrystals with three variants as already observed by Nakagomi [6]. These nanocrystals can reduce the carrier mobility and explain partly the difference in conductivity with materials grown by other techniques.

Conductive films are however obtained after argon and hydrogen plasma treatments. Conduction is more effective after hydrogen treatment, which confirms calculations by Varley *et al.* [5]. However, Secondary Ion Mass Spectroscopy shows a surface modification of Ga/Sn/O as well as the incorporation of hydrogen over the whole film thickness. At low temperature, the conductivity is controlled by a hopping process [3] and the plasma treatment shows a strong absorption in the visible range. Conductivity after a temperature cycle at 500 K shows an irreversible decrease in conductivity but also an increase in transparency. The effect of Sn concentration, oxygen non stoichiometry (deep level) and hydrogen are difficult to separate but the conductivity seems to be related to a polaron mechanism.

## References

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