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Doping effects on growth and properties of oxygen deficient Ga oxide films

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ABSTRACT

The effects of Sn or In doping on the growth of oxygen deficient Ga oxide have been studied. Like in the case of pure oxygen deficient Ga oxide, nanocomposite films are formed with metallic (Ga and Sn or Ga and In) clusters embedded in a stoichiometric oxide matrix. The synthesis of such clusters is related to the difference in the free energy of formation of the various oxides which leads to the phase separation with formation of metallic clusters. The superconducting transition in the Ga and In clusters was observed as well as their melting and freezing transitions during thermal cycling. This chemically driven phase separation appears as a possible approach for the formation of nanocomposite films with particular transport properties (conductivity).

1. Introduction

A large oxygen deficiency (more than 15% oxygen missing) in Si, Ge, Ga, In and other oxide-based films leads to the formation of nanocomposite films with metallic (or semiconductor) clusters embedded in a stoichiometric oxide matrix [1–6]. Actually, sub-oxides of such elements, which have a sole valency state, are not thermodynamically stable and evolve towards the most stable phases, i.e. the stoichiometric oxide and metallic (or semiconductor) phases. For example, highly oxygen deficient Ga oxide films, i.e. Ga_2O_x with $x < 2.5$, were converted into nanocomposite films through the following phase separation [5,6]:

$$Ga_2O_x \rightarrow (x/3)Ga_2O_3 + (1-x/3)Ga$$

The driving force for this phase separation [7] is the formation of the stable Ga_2O_3 phase which grows at the expense of the remaining sub-oxide which becomes more and more oxygen deficient. In the extreme case, metallic Ga clusters are formed in a stoichiometric Ga_2O_3 matrix. Such nanocomposite films present very specific thermal and transport properties related to the metallic Ga clusters. Indeed, the resistivity curve as a function of temperature showed a metallic behaviour, followed at low T by the onset of a superconducting transition in Ga metallic clusters [5,6]. In addition the melting and freezing of the Ga metallic clusters were evidenced through the changes induced in the resistivity curves [5,6]. Moreover, the presence of such Ga clusters (50 to 100 nm) was also checked by transmission electron microscopy experiments [5,6].

Doping is largely used to modify or enhance physical properties or to induce a new one in oxide films [8–11], and nanocomposite films have been already obtained through the phase separation of oxygen deficient Sn doped In_2O_x (Sn:In_2O_x) films [12]. In this last case the formation of metallic In clusters (about 20 nm) was explained via the classical nucleation theory [13]. In this work we have followed this doping approach and studied the effect of doping elements (Sn or In) on the properties of oxygen deficient Ga oxide films. Sn can be used as a doping element in Ga_2O_3 to induce a high carrier density [8,14], while the band gap of Ga_2O_3 can be tuned by alloying with In_2O_3 [15]. Owing to the possibility to precisely control the oxygen composition in oxide films grown by pulsed-laser deposition (PLD) [16,17], this method was used to grow oxygen deficient Ga oxide films doped with Sn or In with concentration up to 5%, and their physical properties were investigated.

2. Experimental

The pure and doped oxygen deficient Ga oxide films were grown at 400 °C on c-cut sapphire substrates by PLD at the residual pressure of the ablation chamber (10^{-4} Pa). PLD was performed using a frequency quadrupled pulsed Nd:YAG laser (7 ns duration pulses at a 5 Hz repetition rate). Ga_2O_3 ceramic pellets doped (up to 5%) by Sn or In were used as targets. For comparison purposes, a Sn (9%) doped In_2O_3 target was also used for the formation of Sn:In_2O_x films. Pulses in the 50 to 200 MW/cm^2 range irradiated at a 45° angle of incidence these ceramic targets. Further details on PLD process and experimental set up are given elsewhere [18,19].

The thickness and composition of the doped Ga_2O_x films oxide films were determined by Rutherford backscattering spectrometry (RBS), using the 2.5 MeV Van de Graaff accelerator of the INSP. These RBS measurements were undertaken at the SAFIR IBA Laboratory University Pierre and Marie Curie. RBS gave composition with a good accuracy for Ga (1%), while the oxygen content was only determined with a 4%

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accuracy. The resistivity of the doped Ga_2O_x films was measured as a function of temperature (in the 4 K to 350 K range) in the classical four probes geometry.

3. Results

In pulsed-energy beam deposition methods like PLD, the stoichiometry of the oxide films can be controlled by the partial oxygen pressure during the growth and the laser power density [20,21]. In this work, the pure and doped Ga oxide films were grown under vacuum (residual 10^{-4} Pa pressure), and the RBS measurements show the formation of largely oxygen deficient In or Sn doped Ga_2O_x films with x in the 2.3 to 2.5 range, i.e. more than 20% of oxygen atoms are missing. This composition does not mean that a specific chemical phase is present in the films. In fact, in RBS measurements, the absolute numbers of cations and O atoms are determined independently of the nature of chemical phases. This means that the In or Sn doped Ga_2O_x ($x < 2.5$) composition represents an average film composition. The growth conditions (400 °C, 10^{-4} Pa) were those required to obtain nanocomposite films trough the phase separation [6], and this possibility was checked by temperature dependent resistance R(T) measurements.

First let us recall that pure $Ga_2O_{2.4}$ and Sn:$In_2O_{2.4}$ films ($x < 2.5$) undergo a phase separation during the growth leading to the formation of nanocomposite films with metallic clusters embedded in a stoichiometric matrix [4–6,12,13]. Figs. 1 and 2 represent typical R(T) curves for these systems, and show a metallic behaviour followed at low T by a sharp drop in resistance characteristic of the onset of superconductivity in the metallic clusters. For pure Ga_2O_x (Fig. 1) the superconducting transition is not complete (zero resistivity is not reached), the onset of the transition was always only observed, i.e. the Ga clusters are not connected through the film. As shown in the inset in Fig. 1, after the resistance drop, the metallic conductivity is observed for lower T. For Sn:In_2O_x (Fig. 2) the superconducting transition leads to zero resistivity, meaning that a percolation path exists in the nanocomposite films through the metallic clusters. Moreover, in the high T part of these two curves a thermal cycling leads to the presence of a pronounced hysteresis related to the melting and freezing of the metallic clusters. The effects of melting and freezing on the R(T) curves are due to the resistivity of Ga in the solid state which is higher than that in the liquid state [22,23], while it is the reverse for In [24]. From Figs. 1 and 2, it is possible to evaluate the melting point and freezing temperature through the mid-point transition in the curves. These values indicated in the figures are very different from that for bulk Ga (303 K) or In (429 K). This behaviour, i.e. a strong decrease of melting temperature and the presence of a hysteresis cycle, which clearly separates the melting and solidification processes, has been reported in the case of numerous nanoparticles embedded in a matrix [25–27]. In contrast to the freezing and melting of Ga and In clusters, the superconducting transition does not show any hysteresis. Indeed, the melting–freezing transition is related to ordering of atoms while the superconducting transition is related to ordering of charge carriers [28].

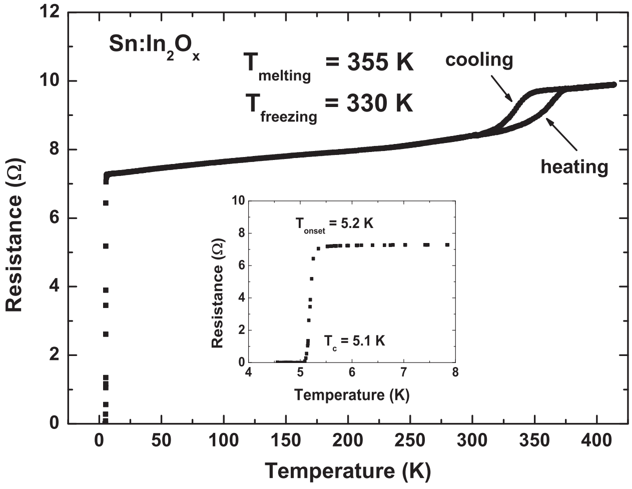

Fig. 2. Temperature dependent resistance R(T) curve for a Sn doped In_2O_x film. The inset shows in detail the low temperature part of the curve.

Oxygen deficient Sn:$Ga_2O_{2.4}$ films behave similarly to the pure $Ga_2O_{2.4}$ films. Actually as shown in Fig. 3 the R(T) curve presents a metallic behaviour followed at about 7 K by the onset of a superconducting transition, but the superconductor state (zero resistivity) is not reached, and a metallic behaviour is observed after the resistance drop (see inset in Fig. 3). Moreover the hysteresis observed between the heating and cooling curves indicates the presence of metallic clusters in the films. From Fig. 3 it can thus be concluded that the phase separation occurs in the Sn doped oxygen deficient Ga oxide films.

Fig. 4 represents a typical R(T) curve for a In:$Ga_2O_{2.4}$ film and shows a metallic behaviour, due to the presence of metallic clusters, followed by a superconducting transition for which zero resistivity is reached. This means that a percolation path is established by the metallic clusters

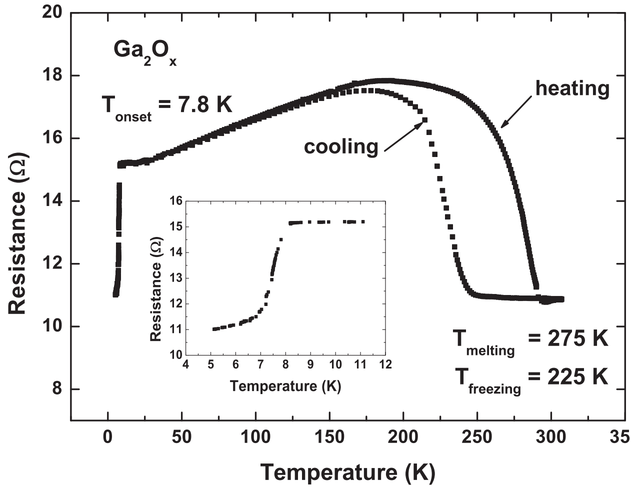

Fig. 1. Temperature dependent resistance R(T) curve for a pure Ga_2O_x film. The inset shows in detail the low temperature part of the curve.

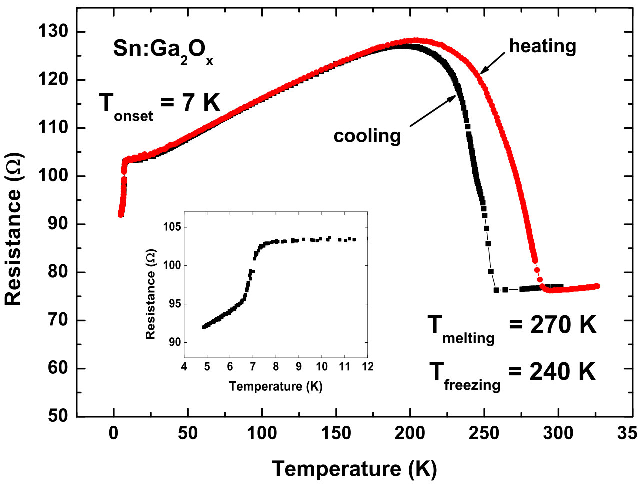

Fig. 3. Temperature dependent resistance R(T) curve for a Sn doped Ga_2O_x film. The inset shows in detail the low temperature part of the curve.