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Red luminescence of Cr in β-Ga_2O_3 nanowires

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Red luminescence emission from chromium doped β-Ga_2O_3 nanowires has been studied by means of photoluminescence (PL) techniques. PL excitation shows several bands in the ultraviolet-visible region. Time decay values, obtained by time resolved PL, at different temperatures fit a three level model with thermal population of the upper level from the middle one. From the results, the origin of the emission is assigned to Cr^{3+} ions in the β-Ga_2O_3 host, and values for the energy level separation and Huang-Rhys factor of the broad $^4T_2$-$^4A_2$ emission are estimated. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2434834]

I. INTRODUCTION

The study of semiconductor oxides is of increasing interest due to their applications in fields such as gas sensing, optoelectronic devices, or transparent conductors. The research on these oxides relates not only to bulk materials but also to low dimensional structures, such as nanoparticles, nanowires, nanodots, nanobelts, or nanocombs, e.g., Ref. 1. In particular, monoclinic gallium oxide (β-Ga_2O_3) emerges as an interesting material because of its good electronic and optical properties, and recently Ga_2O_3 nanostructures, with potential applications in optoelectronic nanodevices, have been developed.[2,3] The reported wide band gap of this oxide, ~5.0 eV, provides the possibility of light emission between the infrared and ultraviolet regions of the spectrum. Investigations concerning optical properties of β-Ga_2O_3 nanocrystals have been typically focused on the ultraviolet-green emission,[3] which has been explained by intrinsic donor-acceptor pair (DAP) recombination.[4] Song *et al.* reported a red photoluminescence (PL) emission at ~1.67 eV in β-Ga_2O_3 nanowires doped with nitrogen,[2] which was attributed to DAP transitions between oxygen vacancy (donors) and a deep energy level due to nitrogen dopants (acceptors). On the other hand, red sharp emission peaks at low temperatures, as well as a broader band at room temperature, were obtained from nano- and microstructures grown by thermal evaporation. The origin of this emission was not determined.[5]

Ga_2O_3 has been studied as a host for transition metal and rare earth impurities to obtain emissions in a wide spectral range.[6] There have also been several reports which show interest in nanostructures doped with this kind of impurities: Cr doped alumina nanofibers,[7] MgO:Mn,[8,9] or MgO:Cr.[9] The well known emissions that these impurities originate are very interesting for optoelectronic applications. Cr^{3+} emissions are well known in several hosts.[10–15] However, few works have been devoted to Ga_2O_3:Cr (e.g., Refs. 6 and 16–18) and the extension of these studies to Ga_2O_3:Cr nanowires would be of interest. Its luminescence has several interesting applications: for example, the broad $^4T_2$-$^4A_2$ emission observed at room temperature is used in other hosts for tunable lasers[11] and could be beneficial in potential Ga_2O_3:Cr lasing nanowires, where amplification wavelength would be selected through Fabry-Pérot modulations due to reflections in the wire ends. In this case, very sharp emissions, such as the Cr^{3+} *R* lines, could not be so favorable.

In this work the red luminescence of chromium doped β-Ga_2O_3 nanowires and submicron size crystals is investigated by steady-state and time resolved photoluminescence (PL) and PL excitation (PLE) measurements. The results confirm that its origin is in the Cr^{3+} ions introduced in the Ga_2O_3 host. From the PL time decay evolution with temperature, a calculation of the energy difference between the ^2E and $^4T_2$ levels of Cr^{3+} ions in this oxide has been performed. The Huang-Rhys factor for the $^4A_2$-$^4T_2$ transition from the PLE spectrum was estimated. These values should be representative for Cr^{3+} in bulk β-Ga_2O_3.

II. EXPERIMENT

β-Ga_2O_3 nanowires and other elongated nanostructures as well as microcrystals were obtained during sintering of Ga_2O_3 powder under argon flow, as detailed elsewhere.[5] Samples were prepared by compacting 99.999% purity Ga_2O_3 powder to form disks of about 7 mm diameter and 2 mm thickness. The disks were annealed on an alumina boat under Ar flow at 1500 °C for 8 or 24 h. Afterwards, the pellets were annealed for 20 h at 900 °C in an alumina boat which contained Cr_2O_3 powders to obtain chromium incorporation through thermal evaporation and subsequent diffusion into the Ga_2O_3. Scanning electron microscopy (SEM) investigations were carried out in a Leica 440 scanning electron microscope. PL and PLE spectra were acquired with a

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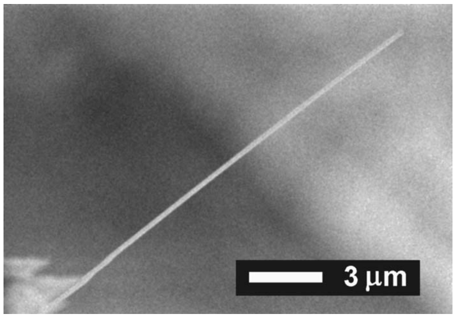

FIG. 1. SEM image of a Ga_2O_3 nanowire grown by annealing under Ar flow for 8 h at 1500 °C.

450 W Xe lamp between 10 K and RT using a closed cycle liquid He system. Time resolved PL (TR-PL) measurements were carried out with a pulsed Xe lamp.

III. RESULTS

Nanowires with sizes from tens to hundreds of nanometers are observed by SEM on the surface of the samples.[5] Figure 1 shows an example of the obtained elongated nanostructures.

Room temperature cathodoluminescence (CL) spectra of the annealed pellets are composed of two broadbands centered at about 2.9 and 3.3 eV, related to β-Ga_2O_3 DAP emission[4] along with an intense red emission at around 1.73 eV.[5] The red CL emission shows at room temperature weak sharp peaks at around 1.80 and 1.78 eV as well, which become dominant when reducing the temperature.[5] PL emission shows a similar behavior, and at 10 K, the only peaks that remained are the one centered at 1.78 eV and its phonon sideband, as observed in Fig. 2 between 1.6 and 1.8 eV.

In order to clarify the origin of the red luminescence, PLE and time resolved PL experiments were performed. The PLE spectrum of the 1.78 eV line acquired at $T=10$ K in the visible and UV regions is shown in Fig. 2. Three main peaks are obtained: one centered around 4.9–5.0 eV, corresponding to the band gap energy of β-Ga_2O_3, and others at 2.88 and 2.08 eV. Figure 2 also shows a Gaussian curve (dashed line) centered at 2.08 eV which approximates the PLE band and which will be discussed below.

Monochromatic TR-PL measurements were performed at temperatures ranging from 10 to 300 K at different wavelengths in the red region. The PL transient for 1.78 eV peak at two different temperatures, $T=10$ and 220 K, from the same area, which is filled with nano- and microstructures, is shown in the inset in Fig. 3. A good fit to a single exponential decay is obtained.

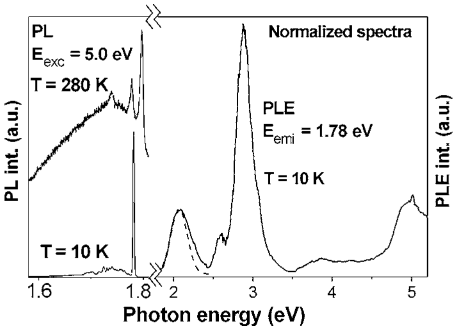

FIG. 2. PL at $T=10$ and 280 K and PLE spectra at $T=10$ K from the nanowire area. The dashed curve is a Gaussian approximation to the PLE 2.08 eV band.

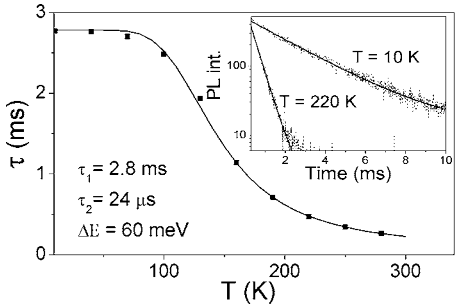

FIG. 3. Evolution of time decay with temperature of the peak centered at 1.78 eV. The dots are experimental results and the solid line is the fit to the three level model, Eq. (1) in the text. Inset: Transients at $T=10$ and 220 K. The dotted curves are experimental results and the solid lines are fits to single exponentials. Excitation energy was $E_{exc}=5.0$ eV.

Figure 3 shows the temperature dependence of the decay times of the peak centered at 1.78 eV. A rather long decay time, 2.78 ms, is obtained at low temperatures. This value decreases when increasing the temperature. Very similar values are obtained for the 1.80 eV peak, not observed at 10 K (Fig. 2) but above around 40 K (see Ref. 5). The dots correspond to values of τ calculated from experimental data. The data were fitted to a simple model considering transitions from two excited levels, separated by an energy ΔE, to a ground level with time decay constants τ_1 for the lower excited level and τ_2 for the upper one.[10,11] These constants are not supposed to vary with temperature. Thermal population of the upper level occurs from the middle one. When this is the case, the effective lifetime τ at $T \ll \Delta E/k_B$ can be expressed as

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{e^{-\Delta E/k_B T}}{\tau_2}, \tag{1}$$

where k_B is the Boltzmann constant. The fit of this model to the experimental data (Fig. 3, continuous line) yields the following values: $\tau_1=2.8\pm0.1$ ms, $\tau_2=24\pm2$ μs, and $\Delta E=60\pm5$ meV. The same values are obtained from the temperature dependence of the time decay for the peak at 1.80 eV.

IV. DISCUSSION

A relatively broad red band centered around the same energy (1.7 eV) in PL spectra from nitrogen doped β-Ga_2O_3 nanowires was assigned previously to DAP transitions with oxygen vacancies acting as donors and nitrogen impurities as deep acceptor levels.[2] However, the properties of that luminescence are not the same as those of our work and we concluded that their origin is different.[5] In other work,[19] absorption results from crystalline β-Ga_2O_3 showed sharp peaks near the band edge with energy differences of 60, 70, and 120 meV. The results were consistent with a confinement model for one-dimensional acceptor clusters with sizes ~3–4 nm acting as quantum wells which result in discrete levels. These clusters were not ruled out as a possible origin of the sharp red peaks we observed[5] based on the energy difference between some of them, but other intrinsic defects or impurities were neither ruled out.

In the samples studied in this work chromium has been introduced in the oxide host as explained above, obtaining a very high emission yield. It is well known that very low concentrations, of the order of ppm, of Cr can result in strong luminescence.[13,20] This ion emits two well defined lines centered at around 1.78 and 1.80 eV, the so-called R lines, due to ^2E-$^4A_2$ electronic level transitions.[13,16] The time decay τ of these lines in this host has been reported to be in the 2–3 ms range at low temperatures,[16] which is consistent with our results. The temperature evolution of τ was studied between 77 and 600 K in bulk chromium doped β-Ga_2O_3 and β-$Ga_{2-x}In_xO_3$ solid solutions grown by the floating zone (FZ) technique.[17] Values of τ in the β-Ga_2O_3 host were of the same order as those presented in this work. However, no measurements at $T<77$ K were shown, which would have allowed the calculation of τ_1, τ_2, and ΔE. Instead, they estimated the activation energy for thermal quenching. The broad red band superimposed on the sharp peaks at room temperature has been observed in bulk chromium doped β-Ga_2O_3 (Ref. 17) as well as in Ga_2O_3 overlayers on GaN substrate[20] and attributed to the $^4T_2$-$^4A_2$ transition of Cr^{3+} impurities in this oxide. This transition is phonon assisted and results in a Stokes shifted broadband.[10,11] It dominates the Cr^{3+} emission at room temperature because of thermal population of $^4T_2$ level from the ^2E. The PLE spectrum in Fig. 2 presents three main bands at around 5.0, 2.9, and 2.1 eV. The first one is consistent with the host interband transition. The other two coincide with two absorption bands observed in Cr^{3+} doped bulk β-Ga_2O_3 (Refs. 16 and 17) and were assigned to $^4A_2$-$^4T_1$ and $^4A_2$-$^4T_2$ transitions in Cr^{3+}, respectively. All these results point to Cr^{3+} impurities as the origin of the red emission in our nanowires. Therefore, the sharp peaks at 1.80 and 1.78 eV correspond to the R lines (^2E-$^4A_2$ transition) and the broadband observed at room temperature corresponds to the $^4T_2$-$^4A_2$ transition. Their relative intensity evolution with temperature (see Fig. 2 and Ref. 5) is explained by the thermal population from ^2E to $^4T_2$, perfectly correlated with the time decay evolution shown in Fig. 3.

Furthermore, from these results we obtain additional information about the Cr^{3+} radiative transitions in this host. Cr^{3+} has been demonstrated to incorporate substitutionally in β-Ga_2O_3 in the Ga^{3+} distorted octahedral sites.[16,21] Sugano and Tanabe[16] studied the influence of a crystal field with octahedral symmetry on the energy levels of transition metal ions, and showed that the energy difference between the ^2E and $^4T_2$ levels depends on the crystal field. For intermediate crystal fields, as is the case in this host ($Dq/B=2.35$),[13,16] the $^4T_2$-^2E energy difference is not large. A value of this energy difference in β-Ga_2O_3 is not directly obtained experimentally from optical characterization. This is due to the strong electron-phonon coupling related to the $^4T_2$-$^4A_2$ electronic transition, which quenches its zero phonon line (ZPL) absorption (luminescence) peak and shifts the band centers to higher (lower) energy. However, from the time decay results (Fig. 3) we can give a good estimation of the $^4T_2$-^2E energy difference in β-Ga_2O_3: $\Delta E=60$ meV. A slightly higher value, 74 meV, was obtained by Vivien *et al.*[22] using a similar method but in a narrower temperature range. This three level model was used by Kisliuk and Moore[10] to explain the temperature evolution of the red Cr^{3+} emission in ruby and emerald and to estimate this energy difference in both hosts. Yamaga *et al.*[11] also studied the temperature evolution of the time decay in different Cr^{3+} doped garnets and obtained this energy difference. They developed a more detailed model for hosts where the energy difference between the ^2E and $^4T_2$ levels is comparable to the phonon energy. In this case, mixing of the ^2E and $^4T_2$ state wave functions occurs and both the sharp R_1 line and broad $^4T_2$-$^4A_2$ band are observed at very low temperatures, even though thermal population of $^4T_2$ level from ^2E is negligible. However, from our results, we conclude that the value of ΔE that we have calculated in β-Ga_2O_3 is not shifted by more than a few meV by those corrections.

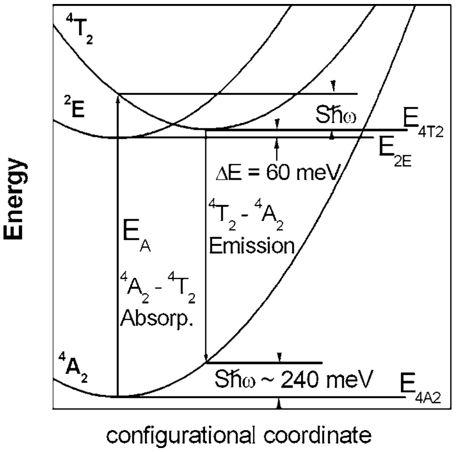

FIG. 4. Qualitative configurational coordinate diagram of Cr^{3+} levels in Ga_2O_3. The parabola minima E_{4T2}, E_{2E}, and E_{4A2} are drawn in the right for clarity.

In order to complete the characterization of the red emission, we sketch the single configurational coordinate (SCC) diagram for the Cr^{3+} energy levels by assuming equal force constants (Fig. 4).

We can also make an estimation of the Huang-Rhys factor S of the $^4A_2$-$^4T_2$ transition of Cr^{3+} in β-Ga_2O_3. At $T=0$ K, the $0\rightarrow n$ transition probability is given by $W_{0n}=S^n e^{-S}/n!$, resulting in an intensity distribution with its maximum displaced from the $0\rightarrow 0$ transition (ZPL). The envelope of the absorption transitions is a Pekarian curve,[13] which is asymmetric, but for moderately high electron-phonon coupling (roughly $S\geqslant 5$), the absorption band shows approximately a Gaussian shape and no ZPL or satellite peaks are observed. It can be shown that, if this is the case, the peak of the absorption band is centered at about $E_A=E_{4T2}$-$E_{4A2}+S\hbar\omega$ (see Fig. 4), where $\hbar\omega$ represents the average energy of the phonons assisting the relaxation.[14] The PLE band at 2.08 eV in Fig. 2 corresponds to the $^4A_2$-$^4T_2$ absorption transition and shows no sharp features and a certain asymmetry. Therefore, we would expect a moderately high value for S. The dashed curve in Fig. 2 corresponds to a Gaussian curve centered at 2.08 eV which represents fairly well the band, although its shape is not perfectly symmetric. From this value of E_A and the estimated one for E_{4T2} we calculate $S\hbar\omega \cong 240$ meV. We can estimate a value for the average $\hbar\omega$ from the PL spectrum at 10 K (Fig. 2). A band composed of a whole set of phonon replica of the R_1 line, corresponding to phonons with different energies, is observed in the spectrum. The center of the band is displaced around 45–50 meV from the R_1 ZPL. It seems reasonable to use its value as an estimation of the average energy of the phonons acting during the $^4T_2$-$^4A_2$ relaxation. Values slightly higher than this one were previously considered for Cr^{3+} in yttrium-gadolinium garnet (YGG) (Ref. 11) and in ruby and emerald.[15] From all this we can estimate $S \sim 5$.

V. SUMMARY

In summary, luminescence spectroscopy has been used to characterize the red emission obtained in chromium doped β-Ga_2O_3 nano- and microwires. This emission is attributed to electronic transitions of trivalent chromium ions in this host. Temperature evolution of the luminescence time decay is well fitted to a three level model where thermal population between the two upper ones occurs. In particular, these three levels are the $^4A_2$, ^2E, and $^4T_2$ of Cr^{3+}, and a value of 60 meV is obtained for the $^4T_2$-^2E energy difference in this oxide. A rough estimation of the Huang-Rhys factor for the $^4T_2$-$^4A_2$ electronic transition in this host yields a value of $S \sim 5$.

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