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The optical absorption edge of nanocrystalline $Ga_{1-x}Mn_xN$ films deposited by reactive sputtering

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Abstract
We have focused on the optical absorption edge of nanocrystalline $Ga_{1-x}Mn_xN$ ($0.00 \leqslant x \leqslant 0.18$) films deposited by reactive RF magnetron sputtering. The films obtained are nanocrystalline with grain sizes of about 25 nm, having wurtzite structure and strong orientation texture in the *c*-axis direction. The optical characterizations of the absorption edges were obtained in the 190–2600 nm spectral range. The increase of the Mn content causes an increase of the absorption coefficient which can be clearly noticed at low energies, and a quasi-linear decrease of the optical gap. Broad absorption bands observed around ~1.3 and ~2.2 eV were associated with transitions between the Mn acceptor level and the valence and conduction bands, respectively. The observed changes in the optical properties due to the Mn incorporation observed in these nanocrystalline films are similar to those reported for ferromagnetic GaMnN single-crystal films.

1. Introduction

GaMnN is one of the most promising candidates for realization of a room temperature ferromagnetic semiconductor due to its Curie temperature above 300 K [1, 2]. The preparation of ferromagnetic $Ga_{1-x}Mn_xN$ was achieved recently by using the MBE technique [3–6] and has also attracted the attention of several groups [7–9]. It was proposed by different groups [1, 2, 10] that the ferromagnetism in the GaMnN systems is carrier mediated and related to substitutional Mn incorporation in the Ga sites; however, the origin of ferromagnetism in these systems [10, 11], like in other diluted magnetic semiconductors, is still under debate [10–12]. Hence it is very important to understand the electronic interaction between the Mn ions through the GaN lattice, and its dependence on the kind of GaN matrix structure and morphology. Recent studies [13–16] reported the existence of an Mn acceptor level located close to the middle of the gap in ferromagnetic monocrystalline GaMnN. The electronic transitions between this Mn level and the valence and conducting bands have been noticed in optical and electronic experiments [13–16].

Even though films prepared by sputtering are generally amorphous or polycrystalline, recently Guo *et al* [17] have successfully grown single-crystal GaN films at relatively low substrate temperatures using RF magnetron sputtering, bringing considerable interest to the preparation of GaMnN films using this technique. In recent reports we have described the preparation of nanocrystalline $Ga_{1-x}Mn_xN$ films by the sputtering technique and their structural and vibrational properties [18, 19]. Among the advantages of the sputtering technique is the low cost, the generation of fewer residues than in some traditional methods, and the possibility of growing the films at relatively low temperatures resulting in more control on the phase separation during growth.

In the present study we focus on the optical properties of nanocrystalline $Ga_{1-x}Mn_xN$ thin films grown by RF magnetron sputtering. The effects of Mn incorporation on the optical absorption edge were related to the observations of an absorption band related to the presence of an Mn acceptor level inside the band gap.

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2. Experimental details

The films were prepared in an RF magnetron sputtering system on amorphous silica glass (a-SiO_2) substrates maintained at 500 K. The sputtering atmosphere was composed only of N_2 gas (6N purity). Different fractions (0–10%) of the metallic Ga target (7N purity) area were covered by small pieces of metallic Mn (3N purity) to get different values of the Mn content (x values). The deposition details were described in a previous work [18].

The Ga/Mn ratio was measured by electron energy dispersive analysis (EDX), in a Zeiss DMS 960 electronic scanning microscope, while the structural characterization was performed using standard x-ray diffraction analysis [18, 19]. The EDX and XRD analysis indicated homogeneous Mn incorporation into the films, showing no evidence for Mn segregation or significant concentration variations along the films. The films are nanocrystalline, the crystallites having wurtzite structure, mean sizes about 25 nm, and high orientation texture with the c-axes oriented perpendicularly to the substrate surface [18]. The structural properties of the $Ga_{1-x}Mn_xN$ films prepared by sputtering were discussed in detail previously [18, 19].

In the present study, samples of nc-$Ga_{1-x}Mn_xN$ (x = 0.00–0.18) deposited by sputtering onto a-SiO_2 substrates were optically characterized via transmittance measurements at normal incidence at room temperature. A Cary 500 spectrophotometer was used in the 190–2600 nm spectral range. From the transmittance spectra the thickness and the index of refraction of the films were determined using the maxima and minima of interference fringe points and a computational routine based on the Cisneros method [20]. The optically determined thicknesses of the films were confirmed by independent mechanical measurements, made with the help of a profilometer. This computational routine also calculates the absorption coefficient in each maximum and minimum, which will form the low absorption part (at low energies) of the absorption edges. The absorption coefficient in the high absorption part of the spectrum was determined directly from the transmittance data using the calculated thickness and extrapolated values of the refractive index. The coherent multiple reflections in the film and the incoherent multiple reflections in the (finite) substrate are taken into account [20], by using approximation free formulas based on the Maxwell equations.

3. Results and discussion

The transmittance spectra of a set of $Ga_{1-x}Mn_xN$ films with variable Mn content are shown in figure 1. The spectra show the interference fringes in the 0.5–3.0 eV range while the absorption edge is clearly noticed in the 3.0–4.5 eV range. For films in which $x \leqslant 0.05$, the interference fringes present a good regularity, indicating good optical homogeneity, while for samples with Mn content $x \geqslant 0.07$, the interference fringes are smoothed by the effect of the increasing absorption. The $x = 0.18$ film did not present clear interference fringes because of its high value of absorption coefficient even in the low energy range. The optically calculated thicknesses of the films, confirmed by profilometer measurements, were in the 600–700 nm range, resulting in an almost constant deposition rate of about 1.3 Å s^{-1}. The static refractive index (not shown) displays an overall increase with the Mn content from 1.9 in the pure GaN sample to 2.3 in $x = 0.18$ sample.

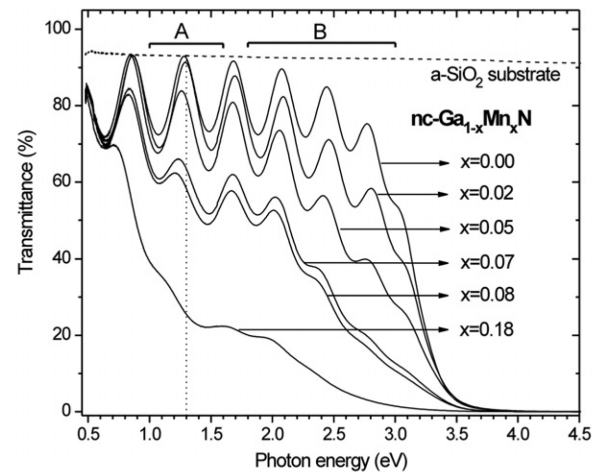

Figure 1. Transmission data for the nc-GaMnN films. The dashed horizontal line shows the transmittance data of the amorphous silica substrate. The dotted vertical line shows the centre of the region (1.1–1.6 eV) where an absorption band is identified, corresponding to a decrease of the maximum and minimum transmittance intensities for $x > 0.05$ films.

The absorption edges, calculated from the transmittance spectra, are shown in figure 2. The pure nc-GaN film presents a more abrupt increase of the absorption than the amorphous GaN (a-GaN) [21] but less steep than the monocrystalline one (c-GaN) [8, 22], as we could expect from a nanophase material, which has many sources of electronic disorder such as lattice distortion and tension, wrong bonds and dangling bonds, which are present mainly in grain boundaries. This electronic disorder implies broadening of the valence and conducting bands and the appearance of a considerable density of tail states at the edges of these bands. This fact is manifested by an increase of the sub-gap absorption and a decrease of the optical gap from 3.4 eV for monocrystalline GaN [22] to 3.2 eV for our nc-GaN as determined from E_{04}.

Focusing on the effects of the Mn incorporation, figure 2 shows that the increase of the Mn content causes an overall increase in the absorption spectra of the GaMnN films, mainly at energies smaller than the gap. The increase of the absorption coefficient is reflected in a quasi-linear decrease of the optical gap (E_{04}) from 3.2 to 2.4 eV in the $0 < x < 0.08$ range and further to 1.3 eV at the $x = 0.18$ extreme (inset in figure 2). Note that the GaMnN film with the highest Mn content ($x = 0.18$) presents a very strong absorption for energies above 0.75 eV, indicating a significant reduction of the band gap ($E_{04} = 1.3$ eV) and the creation of a relatively high density of defect states inside it.

On the absorption edges of films with $x \geqslant 0.05$ it is worth noting the existence of a bump centered at ~1.3 eV. Correspondingly a decrease in the mean transmittance value is noted in the 1.0–1.6 eV energy range (region A in figure 1).

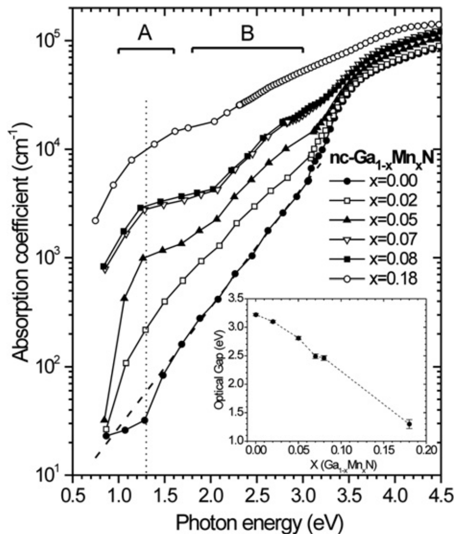

Figure 2. Absorption edges of the set of nc-GaMnN films prepared by sputtering. The dashed line represents the Urbach line traced in the GaN low energy absorption. This dashed line was also used to normalize the absorption edges of the Mn containing samples at low energies (dashed lines in figure 3). The inset shows the decrease of the optical gap (E_{04}) with the Mn content (x).

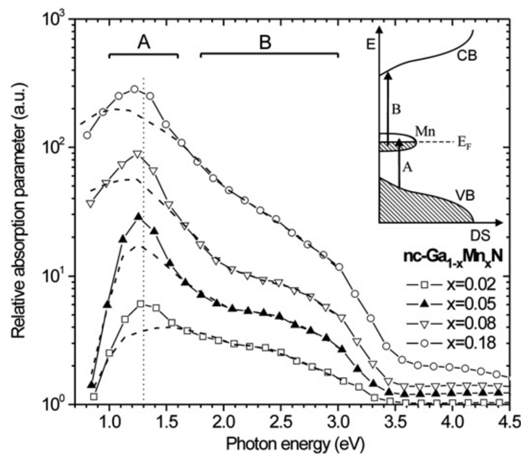

Figure 3. Relative absorption parameter of the Mn containing samples obtained by dividing the absorption edges of these samples by the absorption edge of the GaN pure film. The dashed lines correspond to use of the linear interpolation of the Urbach (dashed line of figure 2) edge as the reference.

A smaller and broadened absorption bump is also noted at energies between 1.8 and 3.0 eV for the films with $x = 0.07$, 0.08 and mainly in $x = 0.05$. In order to obtain a better view of this absorption structure, in figure 3 we have plotted the relative absorption parameter for the set of films. This parameter was obtained by dividing the absorption coefficient of the Mn containing samples by the absorption coefficient of the pure GaN sample ($x = 0.00$). In this figure we can note that all GaMnN samples show an absorption band centered at ∼1.3 eV (band A) convoluted with a broad band that ends around 3.0 eV (band B).

A similar absorption structure was reported for monocrystalline $Ga_{1-x}Mn_xN$ films [13, 14, 16]. The reported results describe a well defined absorption peak centered at 1.5 eV (band A) and an absorption shoulder that initiated at ∼1.9 eV (band B). Both bands were attributed to the existence of a deep Mn related level; nevertheless the detailed process that causes this absorption is still under discussion. Some authors [13, 16] attribute the band A to transitions from the valence band direct to the Mn^{2+} acceptor level located at $\sim E_V + 1.5$ eV and band B to transitions from this level to the conduction band (see the inset in figure 3). Other groups [14, 15], however, assign the absorption band A to internal Mn transitions, and band B to transitions between the occupied $Mn^{3+/2+}$ acceptor level and the conduction band.

Figure 3 does not allow quantitative analysis, but it is clear that the energy where the band A reaches its maximum is close to (or below) 1.3 eV. If we consider that the band A is governed by transition from the valence band to the Mn acceptor level, the difference between the band A maximum location observed for the monocrystalline (1.5 eV) [13, 14, 16] and that for our nanocrystalline (1.3 eV) GaMnN is consistent with the difference between the gap energies of these materials (3.4 and 3.2 eV respectively). The lower gap energy of the nanocrystalline $Ga_{1-x}Mn_xN$, as discussed above, involves enlargement of the valence band due to the disorder present in this material, which can decrease the distance (energy) between the valence band maximum and the Mn acceptor level.

In the same way, the relatively high disorder in the vicinity of the Mn ions in nanocrystalline GaMnN, represented by small distortions of the bond length and angles, may set the Mn ions under slightly different chemical potential conditions through the lattice. This fact may contribute to the broadening of the Mn acceptor level, which can also decrease the distance in energy between the valence band and this level, contributing to shifting the band A maximum to low energies and to broadening the absorption band structure, as we can see for our results when compared to those observed for monocrystalline GaMnN [13, 14, 16].

So, we propose that the Mn incorporation in nanocrystalline $Ga_{1-x}Mn_xN$ prepared by sputtering is responsible for the creation of an Mn acceptor level located close to the middle of the GaN gap at $\sim E_V + 1.3$ eV, like that occurring in monocrystalline $Ga_{1-x}Mn_xN$. Considering that this Mn acceptor level is semifilled (see the inset in figure 3), we can attribute the absorption band structure to transitions from the valence band to this Mn level (region A) and transitions form this level to the conducting band (region B).

Even though the $Ga_{1-x}Mn_xN$ films prepared by the sputtering technique have polycrystalline structure, and consequently a considerable density of defects, the present analysis shows that the Mn incorporation in these films plays a similar role in their optical properties when compared with those observed for monocrystalline GaMnN films. Also, the structural and vibrational properties of these films reported elsewhere [18, 19] indicate that Mn incorporation occurs mainly in the substitutional Ga sites. These evidences show that the $Ga_{1-x}Mn_xN$ prepared by the sputtering technique is also a good candidate for presenting interesting magnetic properties, such as ferromagnetism near ambient temperature. The magnetic characterization of the material will be addressed in a future work.

4. Conclusions

We have analyzed the changes in the optical absorption edges due to Mn incorporation in nanocrystalline $Ga_{1-x}Mn_xN$ films ($0.00 \leqslant x \leqslant 0.18$) prepared by reactive sputtering. The absorption edge of nc-GaN pure film shows an intermediate behavior, between those of amorphous and monocrystalline GaN. The Mn incorporation was responsible for an overall increase of the absorption coefficient, and for the creation of an absorption band structure inside the band gap. The observed absorption bands were attributed to transitions involving a Mn acceptor band, in analogy with literature results for ferromagnetic GaMnN single-crystal films.

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