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# Visible cathodoluminescence from nanocrystalline GaSb obtained by mechanical milling

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The luminescence of mechanically milled GaSb has been investigated by means of cathodoluminescence (CL) in the scanning electron microscope. Transmission electron microscopy reveals that the GaSb powders obtained after the milling process contain nanocrystals with sizes of few nanometers. CL spectra of the GaSb powders show a bright blue-green luminescence visible to the naked eye, even at room temperature. Furthermore, a shift from blue to green has been observed depending on the milling time. In order to clarify the origin of this visible luminescence, we have performed a CL study on gallium oxide ( $\text{Ga}_2\text{O}_3$ ) and antimony oxide ( $\text{Sb}_2\text{O}_3$ ) powders, which exhibit several emission bands in the visible range. Comparison of these results with CL spectra from GaSb powders shows that oxidation during the milling process of GaSb plays an important role in the luminescence features observed. © 2003 American Institute of Physics.  
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## INTRODUCTION

Different techniques have been employed in the past years to fabricate quantum size particles of semiconductors because of the significant changes that take place in the electronic or optical properties when the dimensions of crystallites approach the atomic scale, compared with those of bulk materials. As an example, a large amount of work has been made in this field since visible luminescence from porous silicon was reported by Canham.<sup>1</sup> In most cases, the luminescence properties of nanocrystalline semiconductors have been explained in terms of the quantum confinement model due to the small size of the nanocrystals embedded in different host matrices.<sup>2,3</sup> Most of the results reported refer to silicon and other indirect gap semiconductors while there are few works concerning narrow gap semiconductors. Among the III–V compounds, GaSb (energy gap of about 0.8 eV) is one of the most intensively studied for optoelectronics and thermophotovoltaic applications.<sup>4</sup> In this work we investigate the possibility of modifying the luminescence properties of this material by producing nanocrystals by means of a ball milling process. This treatment has been employed in other semiconductors, such as Si and Ge,<sup>5,6</sup> to produce nanocrystals showing quantum confinement effects. Cathodoluminescence (CL) studies on undoped bulk GaSb crystals show luminescence bands in the near-infrared range, due to near-band-edge transitions (0.796 eV at room temperature) and to transitions from the conduction band to native defects states (0.777 and 0.756 eV).<sup>7</sup> Recently, visible photoluminescence (PL) studies on GaSb nanocrystals embedded in a  $\text{SiO}_2$  matrix have been reported<sup>8</sup> and the authors attributed the origin of the observed luminescence to the quantum confinement effect.

## EXPERIMENT

An ingot of undoped polycrystalline GaSb was used as starting material for the milling treatments. Milling was performed at room temperature in air or in nitrogen in a centrifugal ball mill (Retsch S100) equipped with a hardened steel vial and 20-mm-diam agatha balls. GaSb powders have been obtained after milling times of 10, 15, 20, and 40 h. Transmission electron microscopy (TEM) observations were carried out with a JEOL 4000 FX microscope operating at 400 kV. The samples were prepared by dispersing the powder in ethanol and separating ultrasonically the agglomerates. A drop of the suspension was then deposited to dry on a thin carbon film supported by a standard TEM grid.

For the scanning electron microscopy (SEM) observations Hitachi S-2500 or Leica 440 scanning electron microscopes were used. The powders were deposited on silver paint on the microscope specimen holder and observed in the secondary electron and CL modes with a beam energy of 20 keV at temperatures between 300 and 90 K. The CL measurements were carried out in the visible range with a Hamamatsu R928 photomultiplier and a charge-coupled-device Hamamatsu PMA-11 and in the near-infrared range with a cooled ADC germanium detector. In order to clarify the possible influence of oxides on the luminescence results, 99.999% gallium oxide ( $\text{Ga}_2\text{O}_3$ ) and 98% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) powders provided by Sigma-Aldrich were also investigated.

## RESULTS AND DISCUSSION

The GaSb powders were obtained by ball milling for different times. We labeled the samples M10, M15, M20, and M40, which stands for milling times of 10, 15, 20, and 40 h, respectively, in air, and N20, which refers to milling in nitrogen ambient for 20 h. In order to obtain information about particle size and crystallinity, TEM analysis has been per-

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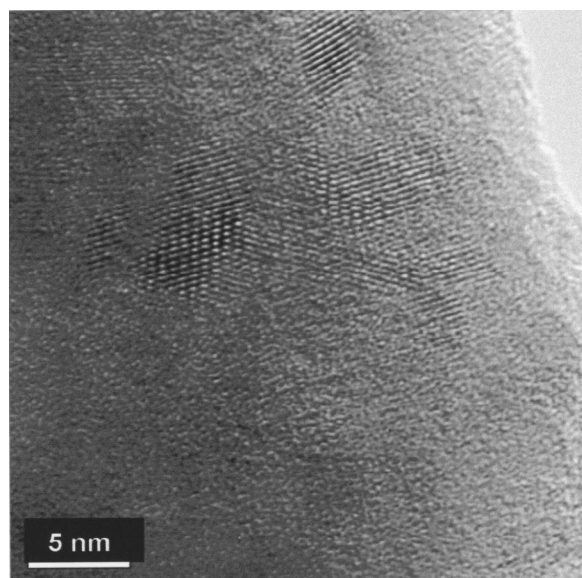


FIG. 1. Transmission electron microscope image from sample M20. The x-ray diffraction from selected areas showed the presence of crystalline GaSb embedded in amorphous material.

formed. Figure 1 shows a TEM image of the M20 sample. It is observed that nanocrystals, with a typical size of a few nanometers, embedded in an amorphous matrix, have been formed after the milling process. The near-infrared CL spectra from milled compared with as-grown GaSb is shown in Fig. 2. The near-band-edge emission band is broader in the milled GaSb powders and an emission emerges at higher energies as a shoulder in the CL spectrum. The observed CL spectrum is similar to the electroluminescence spectrum from GaSb nanocrystals in a conducting polymer matrix reported by Bakueva *et al.*<sup>9</sup>

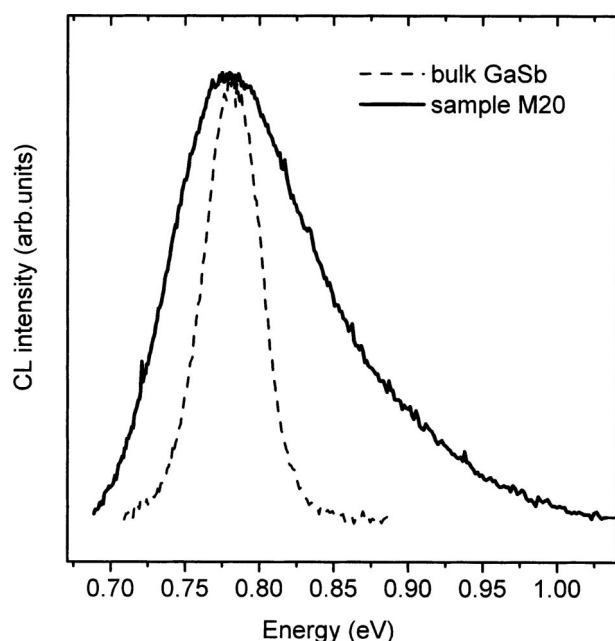


FIG. 2. Cathodoluminescence (CL) spectra in the infrared range from milled GaSb (dark line) and as-grown GaSb (dashed line). The acceleration voltage was 20 kV and the temperature was 90 K.

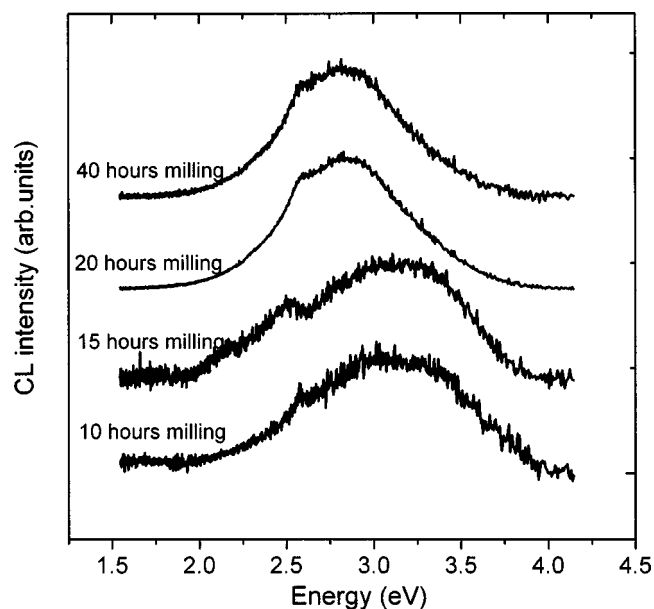


FIG. 3. CL spectra from GaSb powders milled for several times. As the milling time increases the CL emission is redshifted.

The visible CL spectra measured from the different powders just after the milling process are shown in Fig. 3. The main CL emission corresponds to an intense blue band visible to the naked eye, even at room temperature (RT). It can be observed that the emission peak is redshifted from 3.2 to 2.8 eV with increasing milling time. The positions of the CL peaks were not observed to change in the temperature range from RT down to 90 K. The visible CL spectra of gallium and antimony oxides are shown in Fig. 4. The CL observed from  $\text{Ga}_2\text{O}_3$  was more intense than that from  $\text{Sb}_2\text{O}_3$  with the main peak centered at about 2.8 eV [Fig. 4(a)]. On the other hand, the  $\text{Sb}_2\text{O}_3$  emission shows a rather broad band in the visible range and appears to be composed of various peaks, whose relative intensities change by varying the excitation conditions of the electron beam [Fig. 4(b)]. Comparison of  $\text{Ga}_2\text{O}_3$  with milled GaSb reveals that the sample M40 shows a CL spectrum similar to that of  $\text{Ga}_2\text{O}_3$  (see Fig. 5), which indicates that the luminescence of milled GaSb is related to the presence of oxide. Milling in nitrogen atmosphere was performed in order to reduce the oxidation during the process. Figure 6 shows the CL spectra from N20. Only some regions of the sample show luminescence emission and the shape of the CL spectra were found to depend on the excitation conditions in the SEM and the investigated region. The two spectra of Fig. 6 correspond to different excitation conditions in the SEM and show different relative intensities of the present emission bands. The above-mentioned blue-green band appears centered between 3.2 and 3.0 eV and a red emission is observed at 1.7 eV. This emission also appears in the CL spectrum from  $\text{Sb}_2\text{O}_3$  shown in Fig. 4(b). This indicates that by milling in  $\text{N}_2$  atmosphere, oxidation is reduced but cannot be completely avoided, and both the kind and the degree of oxidation responsible for the luminescent features, are different to the case of milling in air.

The redshift observed in CL spectra as the milling time increases can be explained by taking into account previous

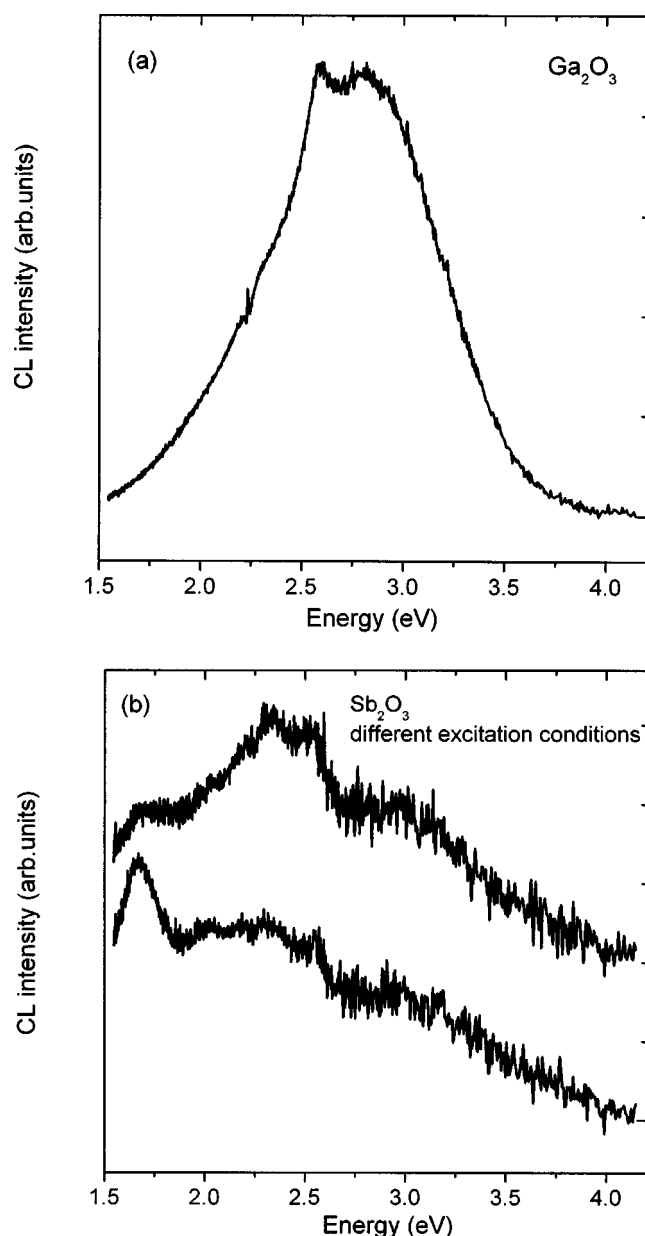


FIG. 4. (a) CL spectrum from gallium oxide and (b) CL spectrum from antimony oxide.

works on gallium oxide.  $\text{Ga}_2\text{O}_3$  is a wide-band-gap semiconductor with an energy gap of about 4.8 eV. Both PL and CL emission of  $\text{Ga}_2\text{O}_3$ , from the ultraviolet to the green spectral region, have been reported.<sup>10–12</sup> On the other hand, there are few reports on the characterization of the optical properties of antimony oxide. The absorption edge of the material at around 4.2 eV has been previously measured, but no luminescence studies have been performed. Some works concerning luminescence studies on  $\text{Ga}_2\text{O}_3$ , reported a blue-to-green shift in PL and CL spectra by increasing the oxygen content in the growth atmosphere. This phenomenon is explained by considering that the blue emission is related to the presence of oxygen vacancies, while the green emission becomes dominant when formation of gallium vacancies occurs.<sup>11</sup> In our case, the observed visible luminescence may be due to GaSb oxidation during the milling process. As a longer mill-

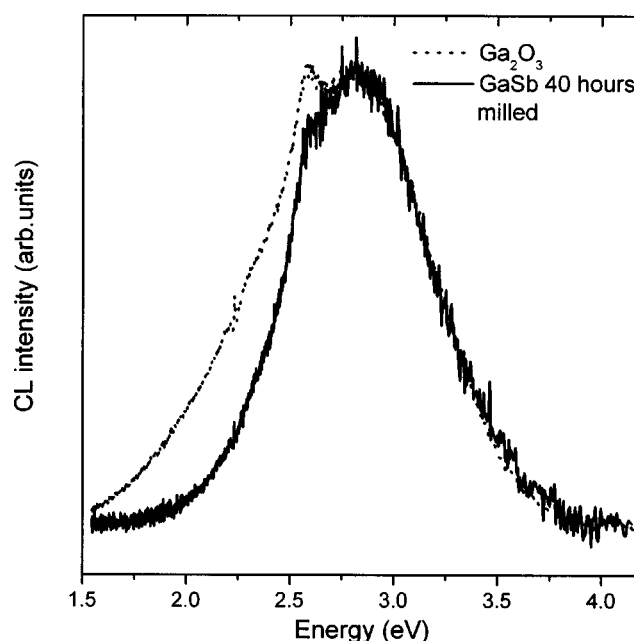


FIG. 5. Comparison of CL spectra from sample M40 and  $\text{Ga}_2\text{O}_3$ .

ing time should correspond to a stronger oxidation, the oxygen incorporation would be responsible for the gradual increase of the green emission intensity. In order to verify this hypothesis, a CL spectrum of sample M15 was acquired several days after the milling process, and a blue-to-green shift was observed (Fig. 7). Furthermore, it can be seen that the CL spectrum of the aged sample is very similar to that of M20, suggesting that the oxidation process goes on after the milling process, and indeed, the green emission is related to the oxygen incorporation.

On the other hand, the observed visible CL of the milled GaSb, a narrow-band-gap semiconductor, could have as a possible origin, a quantum size effect of the GaSb nanocrystals. It is worth noting that two recent papers<sup>8,13</sup> reported

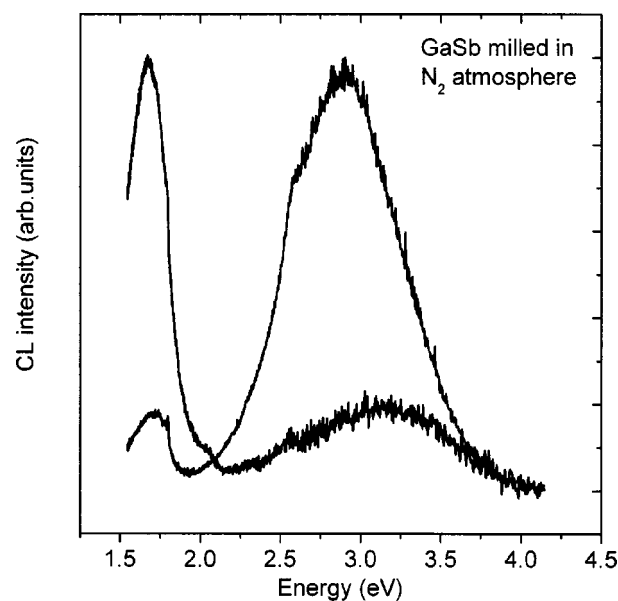


FIG. 6. CL spectra from different regions of sample N20.



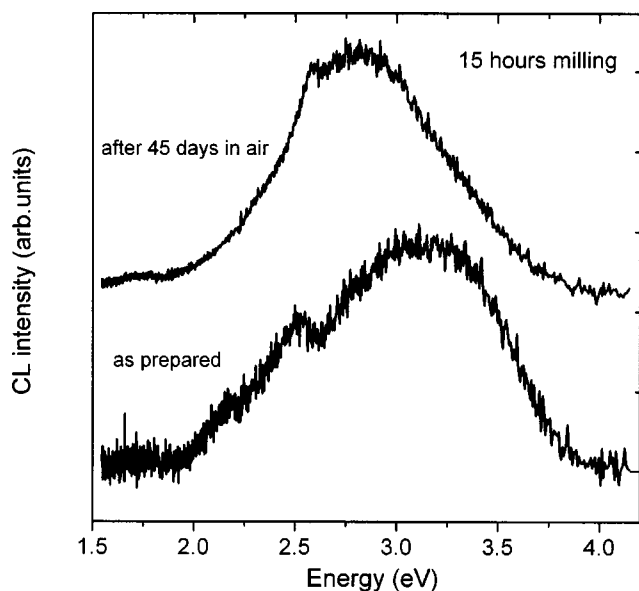


FIG. 7. CL spectra from sample M15 as prepared and after 45 days in air.

visible luminescence from GaSb nanocrystals, obtained by rf sputtering in  $\text{SiO}_2$  and by anodization in HF solution, respectively. In both cases, the authors invoke quantum confinement as the origin of the observed luminescence. In the first work, Liu *et al.*<sup>8</sup> show visible PL emission from nanocrystalline GaSb– $\text{SiO}_2$  composite films in the range 2.3–2.9 eV. They found that the emission was strongly dependent on the particle size and concluded that the PL process takes place across the band gap of GaSb nanocrystals. On the other hand, Sabataityté *et al.*<sup>13</sup> obtained red PL at 1.67–1.85 eV from a porous GaSb layer and assumed that this emission was related to a quantum confinement effect. However, the visible luminescence observed in the GaSb nanocrystals investigated in this work can be explained as arising from gallium and antimony oxide defect states.

## CONCLUSIONS

In conclusion, room temperature visible CL has been observed from mechanically milled GaSb. TEM character-

ization of the milled GaSb powders shows that nanocrystals with sizes of a few nanometers have been formed by the milling process. Our CL spectra of gallium and antimony oxide powders confirm the emissions reported in the literature for  $\text{Ga}_2\text{O}_3$ , while in the case of  $\text{Sb}_2\text{O}_3$  show a complex broad luminescence from blue to red, probably due to the two possible oxidation states of Sb. Comparison of these results with CL spectra from GaSb powders, shows that the presence of oxides is probably one of the luminescence mechanisms in milled GaSb. In particular, the blue-green emission can be explained as arising from gallium oxide defect states, while the lower energy peaks may be due to antimony oxide formation. Moreover, a shift from blue to green can be observed by increasing the milling time of GaSb. This is explained considering that the blue emission is related to the presence of oxygen vacancies, while the green emission becomes dominant when formation of Ga vacancies occurs.

## ACKNOWLEDGMENTS

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