Luminescence properties of transition-metal-doped GaSb

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The luminescence properties of transition-metal (Cr, V, and Ru)-doped GaSb single crystals have been studied by a cathodoluminescence (CL) technique in a scanning electron microscope. Spatial segregation of impurities along the longitudinal direction of the crystals grown by the Bridgman method has been investigated. These dopants suppress the native acceptor concentration to varying extent. The behavior of Ru has been found to be different from the behavior of V and Cr. In particular the complete disappearance of the 777 meV (band A) emission has been observed in GaSb:Ru with a low doping level. A peak at 767 meV is also seen in this sample which, to the best of our knowledge, has not been previously observed in GaSb. The CL results have been complemented by x-ray-microanalysis measurements to ascertain the effect of doping level on the luminescence properties. [S0163-1829(98)05608-2]

I. INTRODUCTION

The transition group metals have a common feature: partial occupancy of the *d* shells. In III-V compounds, this gives rise to several important technological applications and in particular, production of high resistivity materials through transition-metal doping has been widely used. It is surprising to see that there has been an enormous amount of work on transition metals in all III-V compounds except GaSb.[1,2] Until now the only detailed work on transition metals in GaSb was on manganese.[3,4] GaSb is emerging as a potential substrate material for various lattice-matched devices operating in the 0.3–1.6 eV range.[5] Doping of GaSb has been studied by a few groups, however, its study is still in its infancy. However, significant progress needs to be made to completely understand the behavior of impurities in GaSb. As-grown GaSb is always *p* type in nature due to the native acceptors, which are gallium vacancies and gallium on antimony sites (antisites). Reducing the native acceptor concentration has been the challenge of the last three decades. The main method of reducing the native acceptor concentration has been to employ low-growth temperatures in epitaxial techniques.

In the present work, we investigate the effect of transition metals (chromium, vanadium, ruthenium) on the native acceptor concentration. The donor or acceptor nature of the transition metals is difficult to ascertain. The transition metals will form either deep donor levels or deep acceptor levels which will trap charge carriers and give rise to high resistivity as in other III-V compounds. As we have mentioned there is a lack of data regarding the behavior of transition metals in GaSb. For defect characterization, cathodoluminescence (CL) in the scanning electron microscope (SEM) has been extensively applied to many semiconductors and semiconductor heterostructures. This technique which provides information on the nature and spatial distribution of the defects has been to our knowledge, only recently applied to characterize GaSb crystals as reported in previous works of our laboratory.[6,7]

II. EXPERIMENT

The samples studied in this work were GaSb:Cr, GaSb:V, and GaSb:Ru crystals grown by the vertical Bridgmann

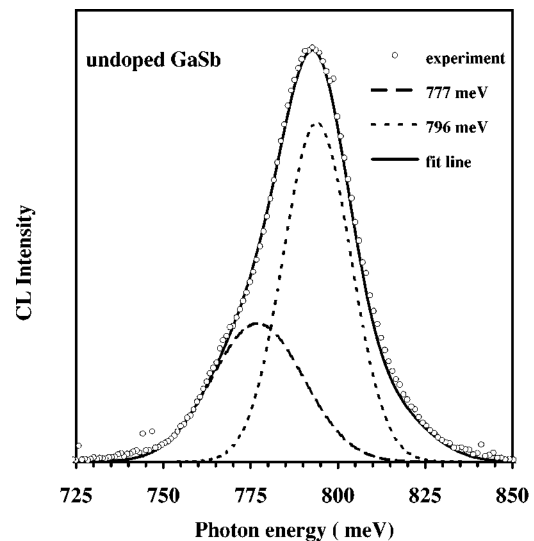

FIG. 1. CL spectrum of an undoped reference GaSb sample grown by the vertical Bridgman technique.

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TABLE I. Positions peaks at 77 K obtained from CL spectra in the different samples studied in this work. Data are in meV.

GaSb:Cr			
sample Cr1	sample Cr2	sample Cr3	sample Cr4
795	798	796	800
770	777	775	777
GaSb:V			
sample V1	sample V2	sample V3	sample V4
807	807	801	795
		778	775
GaSb:Ru			
sample Ru1	sample Ru2	sample Ru3	sample Ru4
777	793	792	790
768	767	767	784

method by tip nucleation without a seed (see Ref. 5). The doping of the crystals was done by adding the respective metals to the melt at the level of 10^{19} cm^{-3}. There is no solubility data for these metals in GaSb. Due to the preliminary nature of the work, the solubility was not investigated in any detail. The crystals were 12 mm in diameter and 40–50 mm in length. After the growth, from each crystal four disks were cut at various places along the length of the ingot and the wafers were chemomechanically polished to a mirror finish. Spatial and spectral CL measurements were carried out on these wafers. The samples are labeled with the symbol of the dopant metal (Cr,V,Ru) followed by a number from 1 to 4 along the growth direction, corresponding to the bottom and to the top of the crystal.

The CL measurements were carried out using a Hitachi S-2500 scanning electron microscope at 77 K and at accelerating voltages of 20–30 kV. The details of the experimental setup for spectral and panchromatic CL measurements are presented elsewhere.[8] In order to study the composition of some of the features observed in the SEM micrographs, mapping of the elements Ga, Sb, Cr, V, and Ru was done by energy dispersive x-ray microanalysis in a Jeol JXA-8900 M superprobe.

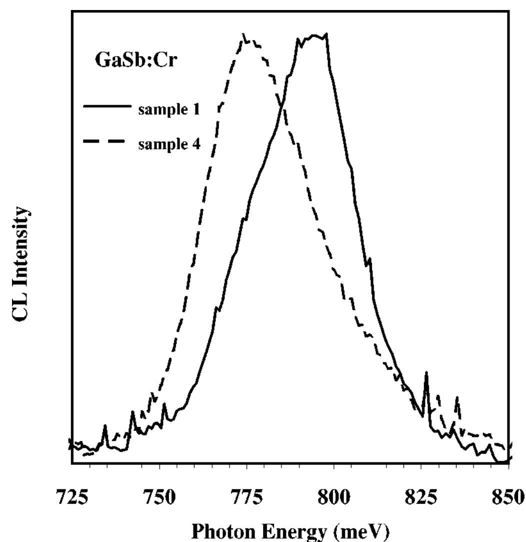

FIG. 2. Evolution of CL spectra in GaSb:Cr along the growth direction.

III. RESULTS AND DISCUSSION

The CL spectrum of an undoped GaSb sample is shown in Fig. 1. The dominant transitions for the undoped sample take place at 777 and 796 meV. Undoped GaSb is *p* type in nature with intrinsic acceptors formed by gallium vacancies (V_{Ga}) and gallium antisites (Ga_{Sb}). These acceptors induce a luminescence band at 777 meV usually called[9] band A. The 796 meV band corresponds to the band to band transition at 77 K. It has been found that GaSb grown from Sb-rich melts has a lower concentration of native acceptors than GaSb grown from stoichiometric or Ga-rich melts, leading to a decrease of the 777 meV peak in photoluminescence (PL) spectra.[10] The luminescence from the doped samples is described in the following sections. In order to compare the obtained results we present in Table I the CL emission bands detected in the different doped samples. These transitions have been determined from the best fits to experimental CL spectra using a sum of Gaussian line distributions obtained by the Jandel Scientific PEAKFIT program.

A. GaSb:Cr

Our previous investigations of GaSb:Cr samples showed the existence of impurity segregation during the growth process in the Bridgman method.[11] The segregation coefficient is lower than unity in these samples, leading to higher Cr concentration in the sample labeled Cr1 and the lowest concentration in sample Cr4.

The incorporation of Cr affects the native defects in GaSb in the following way: native defect creation is believed to be initiated during the growth process by the volatilization of Sb with formation of Sb vacancies. This leads in a further step to the formation of Ga-antisites according to the scheme $Ga_{Ga}+V_{Sb}\rightarrow Ga_{Sb}+V_{Ga}$. With the incorporation of Cr, however, the complex Cr-V_{Sb} is formed similar to the complex Mn-V_{Sb} in GaSb:Mn, which has been observed by photoluminescence and electron spin resonance.[12] According to these assumptions, it is possible to reduce the native defect concentration by doping with Chromium. Our results confirm these suggestions. We observe that the intensity of the native acceptor band A increases along the growth direction with decreasing Cr content. Figure 2 shows the evolution of CL spectra from sample Cr1 to Cr4 in GaSb:Cr. The band A is weak or absent in the sample Cr1, where the Cr concentration is highest, and is dominant in sample Cr4, where the Cr concentration is lowest. The 796 meV CL band corresponds to near band edge recombination at 77 K. Evolution of the CL spectra with increasing temperature in these samples shows a shift to lower energies of the band A peak position, as well as of the fundamental emission.

The different degree of the incorporation of Cr along the growth direction, is reflected in the CL images obtained from the different samples. In the sample Cr4, the CL image shows a contrast which resembles the CL contrast in undoped samples, i.e., dark contrast of the subgrain boundaries

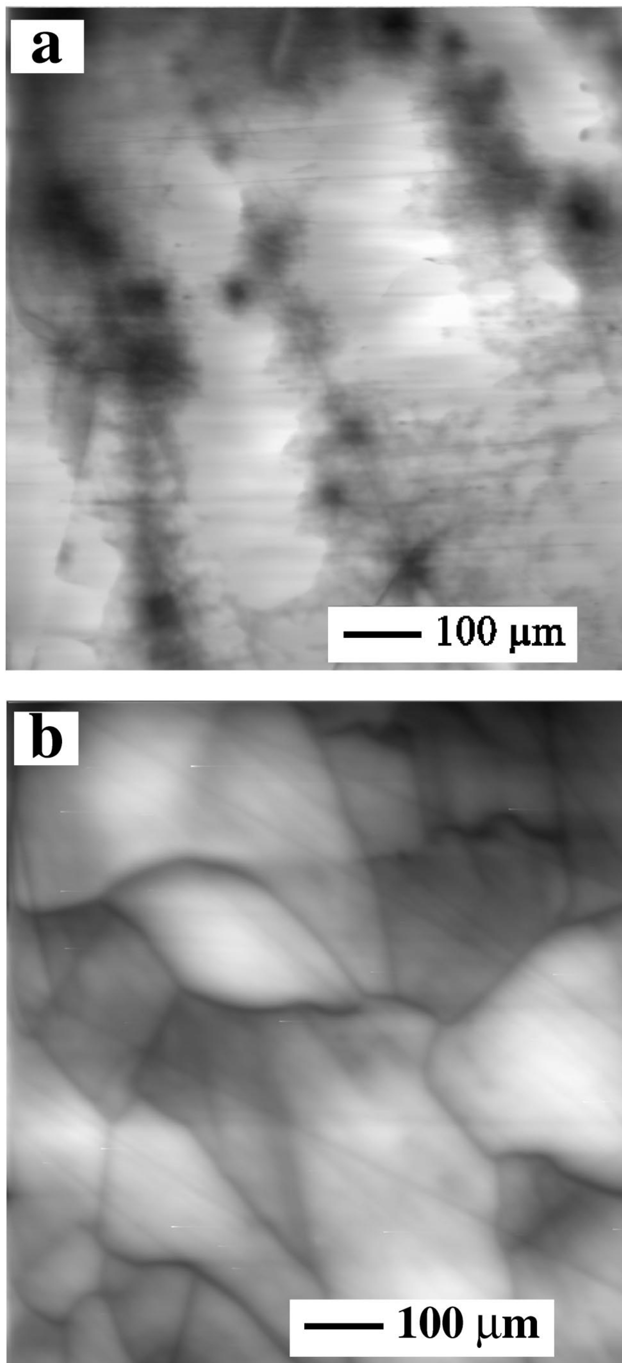

FIG. 3. CL micrographs obtained from GaSb:Cr crystals: (a) sample Cr1 and (b) sample Cr4.

and a uniform appearance in the interiors of the grains.[7] As the concentration of Cr increases in the crystal, precipitates are observed whose number also increases from sample Cr4 to sample Cr1, see Fig. 3.

B. GaSb:V

Figure 4 shows the CL spectra of the V doped samples labeled V1, V3, and V4. In these spectra, an evolution of the emission bands with the same trend as observed in the Cr-doped samples can be seen. The band A is almost nonexistent in samples V1 and V2, the V-rich samples, while in sample V4, corresponding to the vanadium deficient end of the ingot, band A is dominant. Therefore the degree of compensation of native defects, as in the Cr-doped samples, depends on the position in the ingot. In GaSb:V, the peak positions of both CL bands shift to higher energy with increasing V doping (see Table I). This shift may be due to impurity band effect in these degenerately doped crystals.

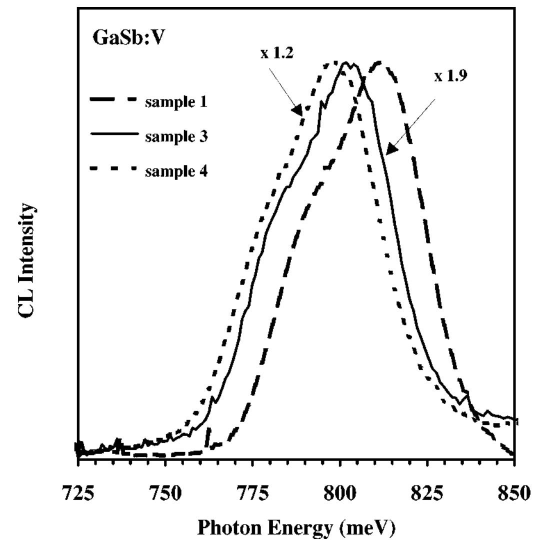

FIG. 4. CL spectra of V-doped GaSb from the different position in the ingot.

CL images of the vanadium-doped samples exhibit a more complex appearance than the CL images chromium-doped samples, but with some common features. Most of the crystal surface appears well smooth and featureless in the secondary electron images. The corresponding CL images are shown in as Fig. 5(a) with dark features at points on the subgrain boundaries. Comparison among the different V-doped samples shows that the size and number of the dark features increase with increasing V doping, suggesting a segregation process at the boundaries.

In some areas of V-doped GaSb it is possible to find topographic features in the secondary-electron image, such as those shown in Fig. 5(c), associated to dark contrast in the corresponding CL image [Fig. 5(b)]. This result indicates a low incorporation efficiency of V in GaSb. In fact, one can clearly see the V inclusions in the crystal. X-ray microanalysis of those regions shows that the protrusions are vanadium rich and, to a lesser extent, antimony rich areas which indicates that they correspond to precipitates with vanadium as the main component. X-ray microanalysis data reveal an atomic percentage of the different elements in the precipitates of 24% Ga, 51% Sb, and 24% V. In precipitate free regions of the sample the V atomic percentage is too small to be observed by x-ray micoanalysis.

C. GaSb:Ru

CL spectra from samples Ru1 to Ru3 reveal a luminescence band centered at 767 meV, which has not been previously reported to the best of our knowledge (Fig. 6). This band is quite intense in sample Ru1, is weaker in samples Ru2 and Ru3, and finally is not present in sample Ru4. This band exhibits a different temperature dependence than the

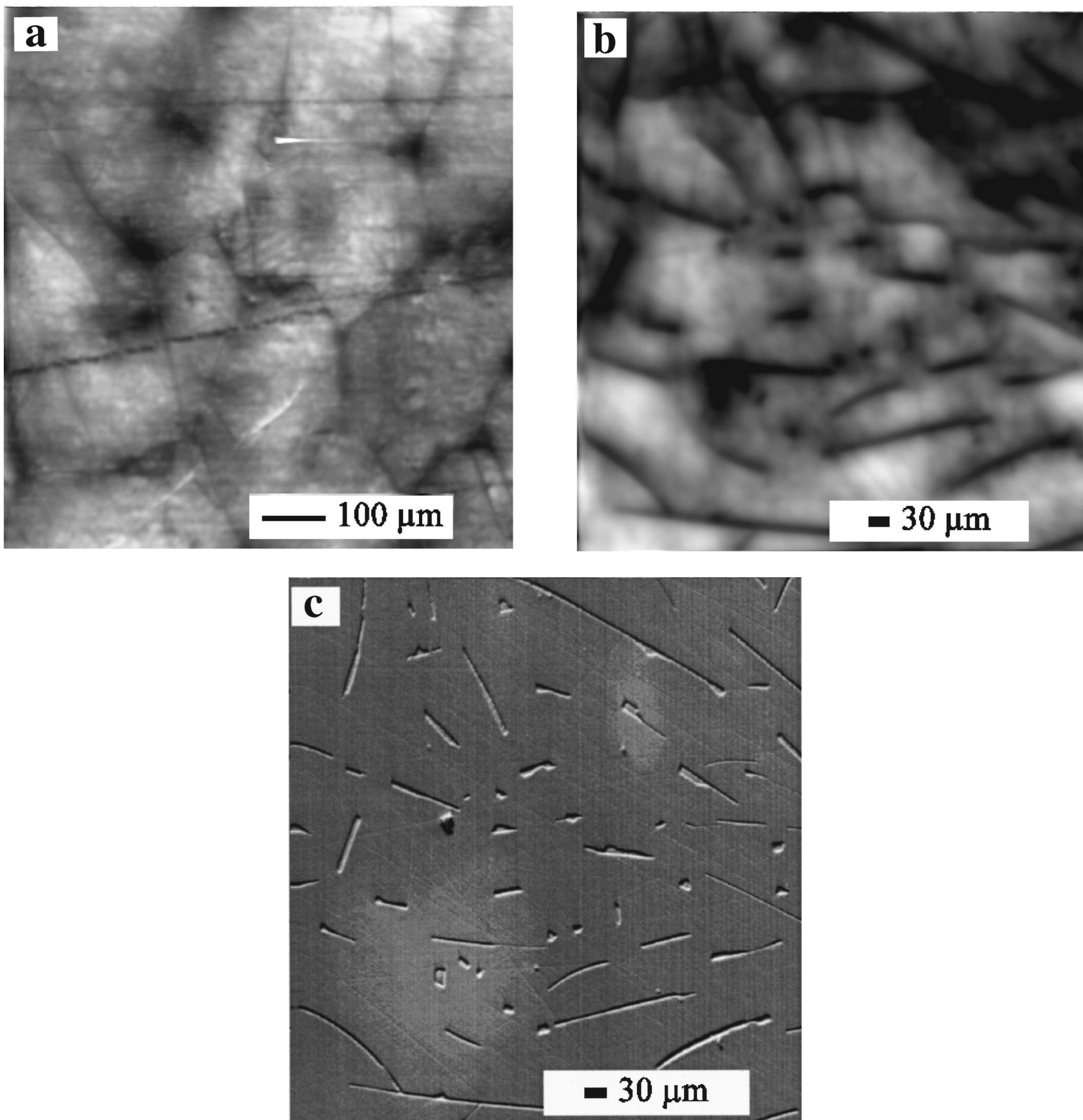

FIG. 5. CL and secondary-electron images of GaSb:V. (a) Representative CL image of the sample V2, (b) CL image of the region containing V-rich features in sample V3, and (c) secondary-electron image corresponding to the same area in sample V3.

other CL bands. Its peak shifts to lower energy as the temperature increases, and the magnitude of the shift is higher than the shift of band A. The fact that the 767 meV band is strongest in sample Ru1 suggests that this band arises from ruthenium, which has the highest concentration in sample Ru1. It is interesting to note that at low levels of Ru, the 777 meV peak (band A) totally disappears. Thus, the way in which Ru affects the native acceptor centers in GaSb is different from the previous studied dopants (Cr,V); Ru is more effective at reducing the native acceptors in GaSb than Cr or V.

In the CL images from samples Ru2 to Ru4 a large number of subgrains of small size (around 100 μm) have been detected in the centers of the disks, whereas bigger and more uniform grains are observed near the edges of the samples. Also near the edges, dark spots, with CL contrast typical of dislocations or precipitates, appear inside the grains. In samples Ru2 and Ru3, a decoration effect of the dark spots is observed [Fig. 7(a)], similar to the often reported haloes surrounding dislocations in CL images of semiconductors.[13] In sample Ru1, the CL contrast reveals an alignment of dark spots following preferred directions [Fig. 7(b)] similar to the

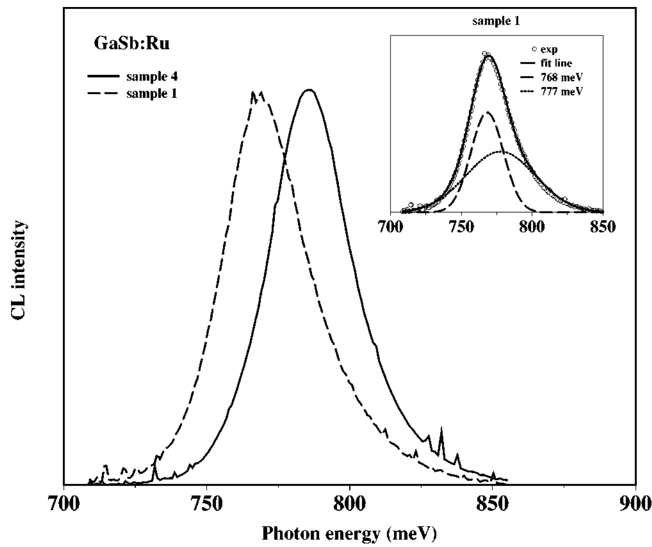

FIG. 6. CL spectra of GaSb:Ru samples. The deconvolution in two bands of the spectrum from sample Ru1 evidences a band at 767 meV as is shown in the inset.

typical contrast of gliding bands in other materials.[13] On the other hand, secondary electron images show that the shape of the precipitates in Ru-doped samples is quite different than in V-doped ones [Fig. 7(c)]. It is possible to distinguish rounded shapes and elongated precipitates. The concentration of these precipitates is highest in sample Ru1 and decreases from samples Ru2 to Ru4. The measured precipitate concentrations range from 5×10^{4} cm^{-2} in sample Ru4, to 1×10^{6} cm^{-2} in sample Ru1. CL images clearly reveal an inhomogeneous distribution in number, shape and size of the precipitates depending on the position along the ingot axis.

X-ray microanalysis data confirm the formation of precipitates, preferentially in sample Ru1, as also occurs in the Cr-doped and V-doped samples. However, the x-ray data reveal that the atomic percentage at the precipitates in the Ru-doped samples is 56% Ga, 33% Sb, and 10% Ru. These samples have an excess of Ga. This excess has been found previously in the literature[14] to enhance the band A emission (Ga-rich material) and on the contrary, Sb-rich stoichiometry leads to a suppression of band A. In our samples, band A is only present in sample Ru1 competing with the band. We believe that the Ruthenium atom has too big a radius to be

FIG. 7. CL and secondary-electron images of GaSb:Ru crystals. (a) CL image of sample Ru3, (b) CL image of sample Ru1, and (c) secondary-electron image of precipitates in sample Ru2.

located at Ga sites, unlike Cr or V atoms, and is thus located at Sb sites in the lattice leading to a Sb deficient matrix.

It should be noted that any precipitate formation means that the solubility limit has been exceeded. Hence even though the concentration of Ru in sample Ru1 is higher, the effective incorporation in the matrix (on lattice sites) is much less. This explains the fact that the 777 meV band (band A) is still observed in sample Ru1. Any change in luminescence spectra due to impurity doping depends on the incorporation of the dopant impurity on lattice sites. Precipitate formation reduces the effect of the impurity on the matrix.

From the present CL and x-ray microanalysis investigations, we conclude that the best method to reduce the native acceptors is with low Ru-doping levels as in sample Ru4, in contrast to the Cr- or V-doped samples where the most effective suppresion of native defects occurs in the impurity-rich end of the ingot (samples Cr1 and V1). To quantify the above statement, it would be necessary to determine the solubility limits of these impurities and their absolute values for segregation, which is not present in the literature to the best of our knowledge.

IV. CONCLUDING REMARKS

Reduction of native acceptors was accomplished by transition-metal-doping in GaSb. In particular, three metals, namely, Cr, V, and Ru, were chosen for technological reasons. The efficiency of impurity incorporation in the lattice was studied by CL spectroscopy and imaging, and by x-ray microanalysis. Impurity segregation coefficients higher than unity for the elements Cr, V, and Ru in GaSb were observed. Further chemical analysis would be required to conclusively determine the absolute values of the segregation coefficients. The complete disappearance of the 777 meV band in GaSb:Ru at low Ru-doping levels was seen. These results are very interesting for potential device applications of GaSb. The appearance of a band at 767 meV in GaSb:Ru requires further investigation to get a better understanding of the interaction between Ru and the native defects in GaSb.

ACKNOWLEDGMENTS

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