Aggregation of Point Defects at Dislocations in III–V Semiconductors

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Abstract

As-grown or freshly created dislocations in n-type GaN and GaAs:S were investigated by Raman scattering and cathodoluminescence microscopy. The free carrier density in GaN decreases from the matrix to the region plastically deformed by indentation. The yellow luminescence (YL) is enhanced around the region of high dislocation density. In contrast to GaN, the free carrier concentration in GaAs:S increases from the matrix to the dislocation since the sulfur donors diffuse to and aggregate at the dislocation. Additionally, also complexes are enriched at the dislocations .

I. INTRODUCTION

Line and point defects influence each other with respect to their structural properties. Their further investigation in compound semiconductors is essential to fabricate high qualitative electronic and optical devices. In this paper, we introduce our recent work on the aggregation of point defects at in-grown or freshly created dislocations in n-type GaN and GaAs. Micro-Raman and scanning cathodoluminescence (CL) microscopy have been applied to characterize various defects or defect complexes aggregated around dislocations.

II. EXPERIMENT

Similar to the former work, our first group of samples of GaN single crystals with a wurtzite structure were grown under high-hydrostatic pressure of nitrogen (15 – 20 kbar) from liquid gallium at a temperature of 1600 °C. The average free electron density is around . The indentation on the N-polar surface were performed at 250 – 350 °C with a 2 N load using a Vickers diamond indenter. The dwell time ranged from 1 to 20 min. After deformation, the samples were cooled down slowly to room temperature. The second group of samples of n-type sulfur-doped (110)-oriented GaAs with a sulfur concentration of were grown by the vertical gradient freeze technique. In order to recognize dislocations at the sample surface, the GaN samples were etched for 1 – 3 min in a molten KOH–NaOH eutectic at 200 – 250 °C. The GaAs samples were etched with a a diluted Sirtl-like photoetching procedure in .

The 632.8-nm line of a He–Ne laser with a power of 25 mW was used for Raman scattering. The laser beam was focused on the sample with a spot diameter of about 1 m. The scattered light was collected and analyzed by a Dilor Labram microscope with a CCD detector. The resolution of spectra was better than . All spectra were recorded in the backscattering geometry at room temperature.

The samples were observed in the secondary electron (SE) and cathodoluminescence (CL) modes in a JSM 6400 or BS 320 scanning electron microscope equipped with an Oxford monochromatic CL system at temperatures between 10 and 75 K. Front-illuminated CCD, photomultiplier, or Ge detectors together with a computer-controlled monochromator were used to measure CL spectra. A 20 kV electron beam energy was selected to excite the sample.

III. RESULTS AND DISCUSSIONS

A light microscopical image of GaN after indentation exhibits a rosette structure and some dark lines in the indentation region (Fig.1 a). The rosette is made of dots which are characteristic of the dislocations revealed by the etching (marked 'D' in Fig. 1a). Our Raman spectra firstly confirm the hexagonal structure of GaN in the matrix because of the existence of the line at (Fig. 1, b-1). Detailed examination of the -like peak in Fig. 1 (b-1) reveals that it is actually located at , below the peak in a perfect GaN crystal. It should be reminded that the peak around reflects the LO phonon–plasmon mode () which is related to the free electron concentration. The measured broad -like peak indicates the degeneration of the and peaks. As shown in Fig. 1 (b-2), the degenerated peak splits into the respective two sub-peaks in the rosette region. In the high-energy part of the spectrum in Fig. 1, a wide-band peak at (labeled EF for convenience) is present (b-1, b-2, b-3). The EF peak has been proven an character. It is well known from doped GaN with a high free electron concentration, consistent with the appearance of the line.

From the matrix to the indentation center, the peak shifts up until it is ultimately obliterated by the peak (from point 1 to 4 marked in Fig. 1). There are two possibilities for the effect. One may be due to an increase in the free electron density and the other one to an increase in the compressive stress. Considering the weakening of the peak and hence the reduction of the free electron density from the matrix to the indentation center, a higher stress should be responsible for the shift up of the peak.

As a second step, CL microscopy has been carried out to further investigate the optical properties of deformed GaN. Fig. 2 shows SE and panchromatic CL images (Fig. 2a and b). The CL image exhibits the following characters: i.) Dark lines corresponding to the rows of etch pits in the dislocation rosette appear in one to one correspondence to the light microscopy or SE images. ii.) There is no resolution of individual dislocations. iii.) A bright region corresponding to a higher CL intensity contrasts the dark center.

Correspondingly, CL spectra have been measured point by point (Fig. 2c). The band edge emission (360 nm) cannot be seen due to the sensitivity limit of the used CCD detector from 400 nm to 1100 nm. In all the cases, the peak around 550 nm is related to the well-known YL band. Combining Raman scattering with the CL results, it is reasonable to assume that the YL band origins from intrinsic defects enriched around the region of a high density of dislocations. From Raman scattering, the matrix is of best crystalline order and thus of a low density of defects, while the indentation center is strongly deformed. Nonradiative recombination centers are produced corresponding to low YL intensities in this region. However, near the dislocations around the indentation center, the crystalline order is accompanied by intrinsic defects like, e. g. nitrogen vacancies (donors) or gallium vacancies (acceptors) created during deformation. They act as radiative recombination centers and contribute to the high intensity of the YL band. Given the indication by Raman scattering that the free electron density decreases from the matrix to the indentation region, preferably acceptors dominate the YL band. It is obvious from Fig. 2b that the YL intensity and thus the density of the produced defects is inhomogeneous.

The combination of Raman and CL microscopy has also been applied to the interaction of sulfur dopants with dislocations in GaAs. Fig. 3a shows two typical Raman spectra recorded in the matrix and at an in-grown dislocation. According to the selection rule, only the TO peak at about is allowed for the Raman scattering from the (110) surface of semi-insulating GaAs. However, due to the doping effect and the electron-plasmon coupling, the selection rule is broken. The LO peak around is split into two sub-peaks, . From the calculation of the position of the peak, the free electron density can be estimated to be in the matrix. It increases from the matrix to the dislocation (Fig. 3b).

It can be concluded from the CL measurements that complexes, which result in a CL peak around 1.27 eV, are formed in GaAs:S. These complexes aggregate at the dislocations, corresponding to the increase in the CL intensity from the matrix to the dislocation (Fig. 3c). The higher CL intensity of the 1.27 eV peak is obtained after normalization of the spectra to the CL intensity of the near-band edge emission to eliminate the influence of the dislocation as non-radiative recombination center. Additional experiments of the aggregation of sulfur at fresh dislocations in GaAs together with the theoretical calculation of the diffusion and drift of impurities in the strain field of dislocations state that the intensity and position of this CL peak depend strongly on the sulfur concentration.

The computer simulation of the microscopic diffusion–aggregation processes based on the diffusion model of the kick-out mechanism elucidates that the formation of arsenic precipitates around dislocations is critical in the aggregation process of defects at dislocations. In this way, the extension of the region of increased free electron density and agglomeration of complexes (Fig. 3 b and c) of up to a diameter of a few micrometers can be explained.

IV. CONCLUSIONS

We have investigated the effect of dislocations on electrical and optical properties of GaN and GaAs by combining Raman scattering with cathodoluminescence microscopy. In GaN, intrinsic defects, most likely gallium vacancies, are formed as a result of dislocation motion in the indentation region. The aggregation of these point defects near the heavily deformed region is responsible for the decrease in the free electron density and for the enhanced yellow luminescence (YL). It cannot be excluded that the native point defects formed during deformation form a stable complex with residual impurities, such as oxygen. Such complexes were discussed to contribute to the YL band.

Contrarily, the free electron density in sulfur-doped GaAs increases from the matrix to the dislocation. The dominating process is the diffusion of sulfur donors to the dislocations. In addition, the agglomeration of compensating complexes at dislocations is observed by CL measurements.

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Figure 1: (a) Light microscopical image of the region around an indentation in GaN. 'D' stands for dislocations and 'C' for crack. (b) Raman spectra of GaN acquired at room temperature at four typical positions marked in (a).

Figure 2: (a) Secondary electron image of the GaN sample showing the region around the indentation. The same region is shown in the panchromatic cathodoluminescence image in (b). The CL spectra obtained from the points 1–6 are given in (c). The experiments were made at 10 K. The CL contrast in (b) is only determined by the YL band due to the sensitivity of the CCD detector used.

Figure 3: (a) Raman spectra in the matrix and around a dislocation in GaAs:S. (b) Spatial distribution of the free electron density. The carrier density in the matrix M was calculated to be), while at the dislocation D). (c) Cathodoluminescence spectra showing the defect band related to complexes taken at three typical positions at a dislocation as indicated in the inset. The inset in (c) is a panchromatic CL image detected by a photomultiplier, whose effective detecting range is from 400 to 900 nm. Consequently, the image comes mainly from near-band edge emission and the dislocation is dark due to the dominating nonradiative recombination.

Figure. 1

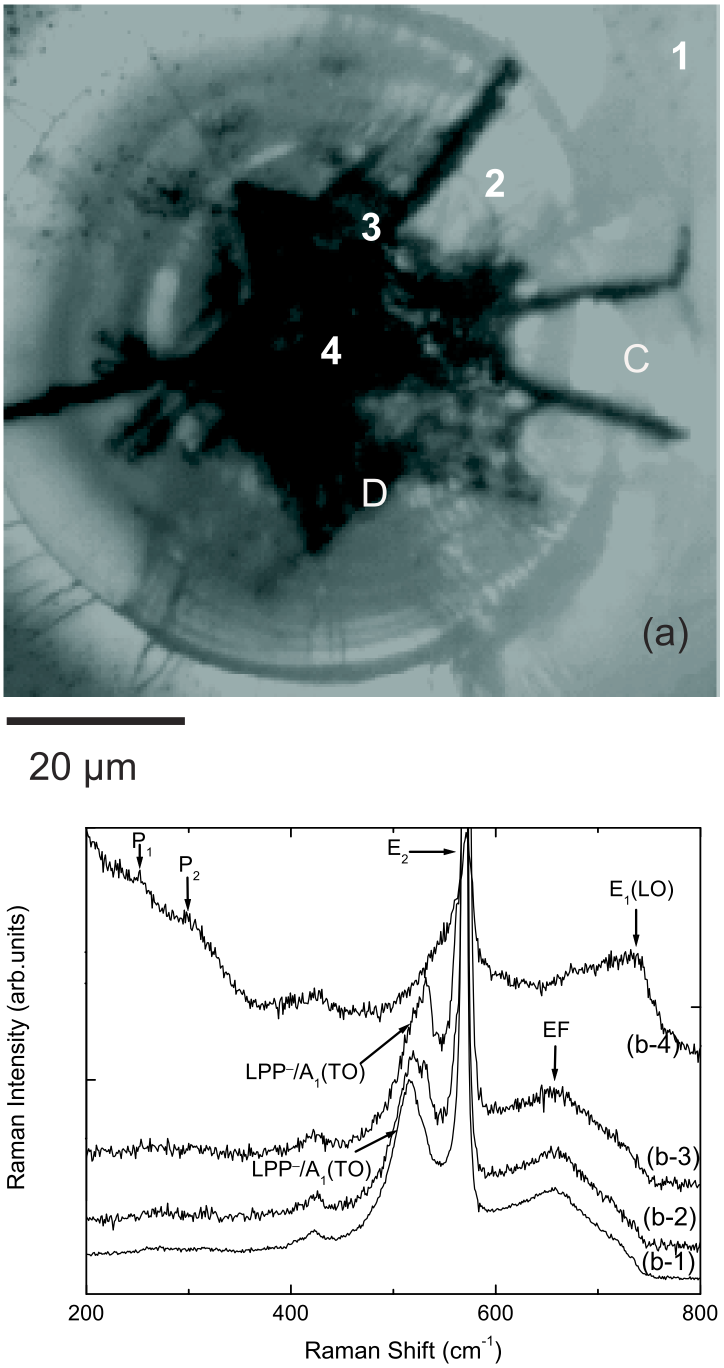

1
2
3
4
C
D
(a)
20 µm
P_1
P_2
E_2
E_1(LO)
EF
LPP$^-$/A_1(TO)
LPP$^-$/A_1(TO)
(b-4)
(b-3)
(b-2)
(b-1)
Raman Intensity (arb.units)
200
400
600
800
Raman Shift (cm^{-1})

Figure. 2

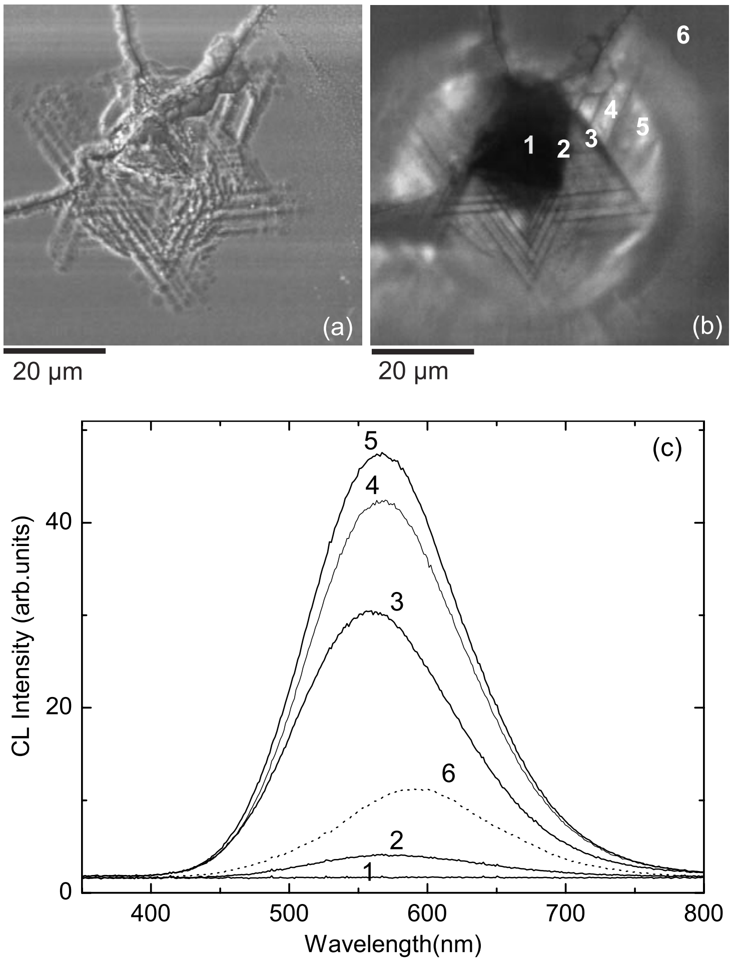
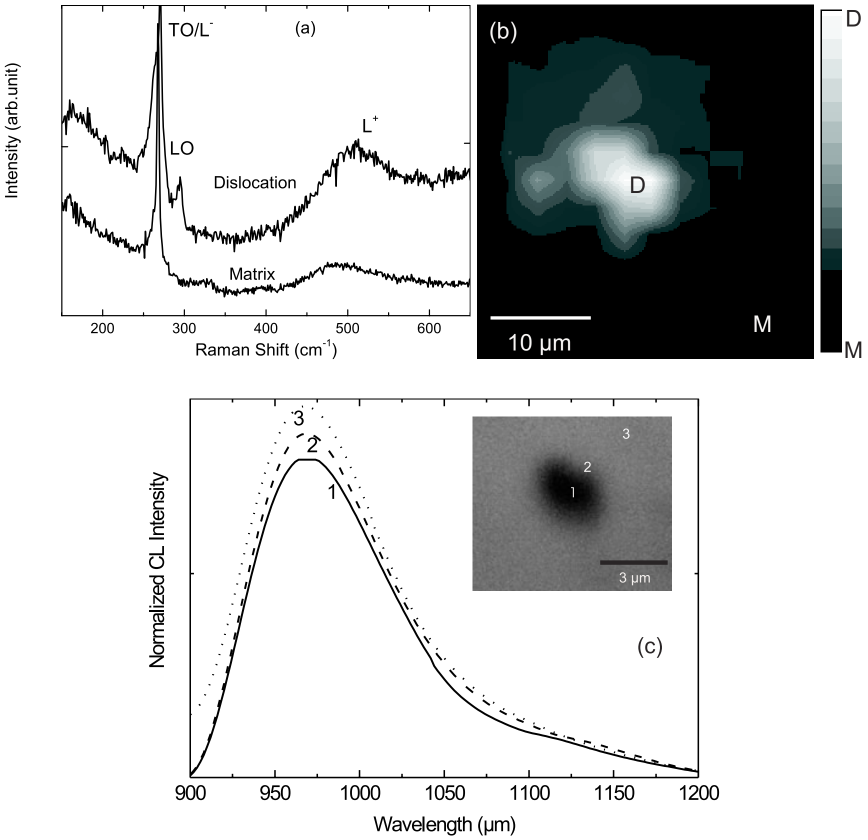

(a)
20 µm
6
4
5
1
2
3
(b)
20 µm
(c)
5
4
3
6
2
1
CL Intensity (arb.units)
0
20
40
400
500
600
700
800
Wavelength(nm)

Figure. 3


TO/L$^-$
(a)
LO
L$^+$
Dislocation
Matrix
Intensity (arb.unit)
200
300
400
500
600
Raman Shift (cm^{-1})
(b)
D
10 μm
M
D
M
3
2
1
3
2
1
3 μm
(c)
Normalized CL Intensity
900
950
1000
1050
1100
1150
1200
Wavelength (μm)