

CHARACTERIZATION OF SEMICONDUCTORS BY PHOTOLUMINESCENCE MAPPING AT ROOM TEMPERATURE

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Room-temperature photoluminescence (PL) mapping technique is used to characterize the distribution of deep levels in semiconductor wafers. The key points to achieve this are a weak excitation condition, high stability of the apparatus, and adequate surface treatment of samples. The deep-level PL associated with the native midgap donor EL2 in semi-insulating GaAs crystals and that associated with the thermal donor (TD) in heat-treated Czochralski-grown Si crystals are detectable at room temperature. The mappings of the EL2-related 0.65 eV band on GaAs wafers indicate a high degree of correlation with the EL2 absorption. Using this technique, semi-quantitative mapping of the EL2 level is realized. The mapping of the TD-related 0.7 eV band shows a characteristic growth-striation pattern, corresponding to the resistivity variation. The present technique makes it possible to evaluate the nonuniform distribution of deep levels in the device-active surface layer of as-received wafers, in air, nondestructively, and with a high spatial resolution.

1. Introduction

Photoluminescence (PL) spectroscopy is widely used to characterize impurities and defects in semiconductors. Generally, the PL measurement at low temperature makes the spectral line very sharp and strong. This is the case for the band-edge PL, such as the PL associated with shallow impurities. A typical example of the PL characterization using the band-edge PL at low temperature is the quantitative impurity analysis in Si, which is now being standardized by American Standards for Testing and Materials [1]. The band-edge PL is detectable at room temperature under the strong excitation condition. Mapping of the band-edge PL has been shown to be useful to characterize the homogeneity of the crystalline quality of semiconductor wafers [2–4]. The technique has great practical advantages of nondestructiveness, high spatial resolution, and the lack of requirement of a special environment (low temperature, high vacuum etc.) for the measurement. However, the relationship between the PL intensity and the crystalline quality is not straightforward.

Deep-level PL spectroscopy has recently been applied to defect analysis in GaAs and Si crystals [5,6], and a direct correlation between deep-level PL and microdefects is beginning to be recognized. The measurement of deep-level PL is not necessarily easy, because this PL is generally weak compared with band-edge PL, and because the sensitivity of the detector is low in the near-infrared region. Therefore, deep-level PL at room temperature has rarely been successful. The author [7] has demonstrated that the measurement of deep-level PL at room temperature is possible in GaAs under a weak excitation condition, using an apparatus of high optical efficiency. The thermal quenching and broadening effects are much smaller in deep-level PL than those for band-edge PL; therefore, the former dominates the spectrum with a spectral shape similar to that at low temperature. This makes the radiative recombination process very simple, leading to the semi-quantitative mapping of defects responsible for deep-level PL. This is a great merit of the deep-level PL mapping technique.

In this paper I will first described briefly the

principle of the method, and then the experimental technique, with special emphasis on the key points which assure achievement of an accurate analysis. I will show two typical examples of deep-level PL mapping in GaAs and Si at room temperature. I believe this is one of the most practical and sensitive techniques yet developed to examine the quality of as-received semiconductor wafers.

2. Principle

The most simplified treatment is described here for the radiative recombination mechanism in semiconductors involving one kind of radiative deep levels. Excess carriers are created in the conduction and valence bands, by the irradiation with light, the photon energy of which is larger than the band gap. Carriers of one type (electrons or holes) recombine directly with those of the other type, or they are trapped first by the deep levels and then recombine with the others. The PL occurs as a result of their radiative recombinations. The exciton luminescence, which often dominates the spectrum at low temperature, is unobservable at room temperature, because the binding energy of the excitons is much smaller than thermal agitation energy.

We assume that the carrier lifetime (τ) is limited by the recombination via “lifetime-killer” centers, and the concentration of the excited carriers (n_{ex}) is larger than the intrinsic carrier concentration and the concentration of the deep levels N_{D} . The intensity of the band-to-band transition (I_{B}) and that of the deep-level (I_{D}) are given by [3,8]

$$I_{\text{B}} \propto n_{\text{ex}}^2 \tau, \quad (1)$$

$$I_{\text{D}} \propto n_{\text{ex}} \tau N_{\text{D}}. \quad (2)$$

Under constant excitation condition, I_{B} is proportional to τ , or inversely proportional to the concentration of the killer centers. This indicates that the variation of I_{B} on a wafer reflects the inhomogeneity of the crystalline quality. The intensity I_{D} is proportional to τN_{D} . If the variation of τ on a wafer is small, the variation of I_{D} reflects the distribution of the deep levels. The effect of surface

recombination and the competition of carrier trapping among multiple centers should be taken into account for a precise analysis. The power law of the variation of the PL intensity with the excitation intensity is square for the band-to-band transition and linear for the trap-related transition. Therefore, the band-to-band PL and the PL associated with the shallow levels are distinguishable by their power law variation, even if they are indistinguishable by their spectral position.

3. Experimental

3.1. Apparatus

The PL measurement was carried out in air at room temperature. The sample was mounted on an X - Y stage with a travel distance of 100 mm for both axes. The travel axes should be parallel to the sample surface to avoid systematic deviation of PL collecting efficiency. The sample was irradiated with the 647 nm line of a Kr ion laser. The beam diameter of the laser was about 0.1 or 1 mm on the sample surface, with an incident power ranging from 0.1 to 100 W cm⁻². The PL from the sample was analyzed with an apparatus of high optical efficiency, consisting of a grating monochromator ($f = 320$ mm, $F = 4.2$) with a 75 and a 600 grooves/mm grating blazed at 2.0 and 1.0 μm , respectively, and Ge and PbS detectors. In order to improve the optical throughput of the system, we made following efforts: (i) the positions of the lenses were computer-controlled depending on the wavelength of the light to correct chromatic aberration, (ii) specially designed aspherical lenses were used to correct spherical aberration, (iii) the gratings and mirrors were coated with gold to improve the reflectivity in the near infrared region, and (iv) multiple filters and shielding plates were used to reduce stray light [7,9,10]. The signal-to-noise ratio of the present apparatus for deep-level PL in the 1.0–2.5 μm wavelength region is nearly two orders of magnitude higher than that of our previous system, which enables the detection of weak deep-level PL.

3.2. Technique

There are three key points in the technique to achieve an advanced deep-level PL mapping. First is the weak excitation intensity condition. As shown in eqs. (1) and (2), the power laws for I_B and I_D are square and linear, respectively. The stronger the excitation intensity becomes, the lower goes the relative intensity of I_D with respect to I_B . Therefore, the trap-related PL is buried in the tail of the band-to-band transition under the strong excitation condition. Furthermore, a rapid intensity change is observed under this condition. An exponential decay was reported for the band-to-band PL in GaAs with a time constant of a few tens of seconds under the excitation intensity of about 1000 W cm^{-2} [3], which is the typical excitation condition reported in the literature [2–4]. In contrast with this, the deep-level PL dominates the spectrum under our weak excitation condition ($\leq 1 \text{ W cm}^{-1}$), as shown typically in fig. 2. This simplifies the recombination process, leading to the semi-quantitative analysis as described later. The PL decay in GaAs was less than 3% for a 10 min irradiation under our weak excitation condition.

The second key point is the stability of the measurement system. The PL mapping on a wafer requires a relatively long time: a few tens of minutes to a few hours, depending on the signal level and the number of data points. The instability of the system induces an artificial pattern. A typical example is shown in fig. 1. This is the band-edge PL mapping on a S-doped InP wafer. Although the intensity looks uniform on the wafer under normal scaling (fig. 1a), a clear growth-striation pattern is revealed under magnified scaling (fig. 1b). In fig. 1b, a 10-step gray scale ranges between $\pm 5\%$ deviation from the mean intensity. These were obtained under a stable condition. Fig. 1c was taken for the same sample under an unstable condition, using the same gray scale. The observed striped pattern is not inherent to the sample, but originates from the periodic change in room temperature.

The third key point is the surface finish of the sample. As reported in detail in a separate paper [11], room-temperature PL is sensitive to the con-

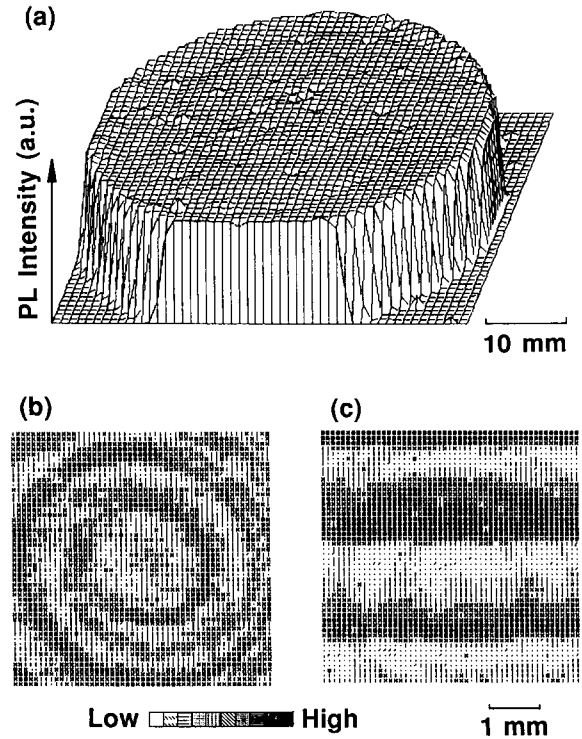


Fig. 1. Mappings of band-edge PL intensity of an S-doped InP wafer at room temperature. (a) Pseudo three-dimensional plot under a stable condition, using a normal intensity scale without zero-offset. (b) Two-dimensional mapping for the same sample under the stable condition, using an expanded gray scale with 10 steps between $\pm 5\%$ deviation from the mean intensity. (c) Two-dimensional mapping under an unstable condition, using the same expanded gray scale. The growth-striation pattern is revealed clearly in (b), while the striped pattern in (c) is artificial.

tamination and damage on the sample surface. The band-to-band PL is found to be more sensitive than the deep-level PL. Use of the water-rinse process prior to the measurement is shown to be very effective in removing the deteriorated surface layer of GaAs wafers. A conventional oxidation is found to be very useful in stabilizing the room-temperature PL of Si wafers. It should be noted that a rub with an ear swab or the plucking marks of tweezers is sometimes strong enough to induce the PL degradation.

4. Results and discussion

4.1. EL2 in GaAs

The native midgap donor EL2 is responsible for the semi-insulating (SI) properties of undoped GaAs crystals [12]. Since the uniformity of the SI properties is of primary importance in device fabrication, a sensitive technique for mapping the EL2 level has been eagerly sought. In this section, the applicability of the PL method for EL2 mapping is demonstrated.

The PL spectrum of an undoped SI liquid-encapsulated Czochralski (LEC) grown GaAs crystal is shown in fig. 2, where the excitation intensity is about 0.1 W cm^{-2} [10]. The spectrum consists of the band-edge emission at 1.42 eV and the deep-level emission at 0.65 eV. The power n in the relationship between the PL and excitation intensities, $I_{\text{PL}} \propto I_{\text{ex}}^n$, is 1.6 for the 1.42 eV band and 0.8 for the 0.65 eV band. This indicates that the two bands are due to the band-to-band and trap-related transition, respectively. Association of the 0.65 eV band with the EL2 level is verified on the bases of the temperature dependence of the 0.65 eV band and of the agreement of the variation on wafers between the PL intensity and the EL2 absorption [7].

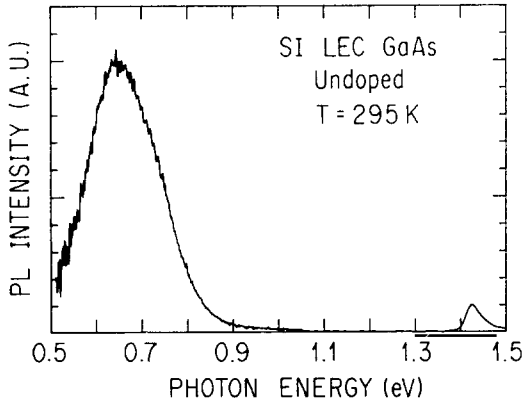


Fig. 2. PL spectrum of undoped SI LEC GaAs at room temperature, under an excitation intensity of about 0.1 W cm^{-2} . The spectral response of the measurement system is calibrated with blackbody radiation. The abscissa and the ordinate are proportional to the photon energy and the number of photons, respectively [10].

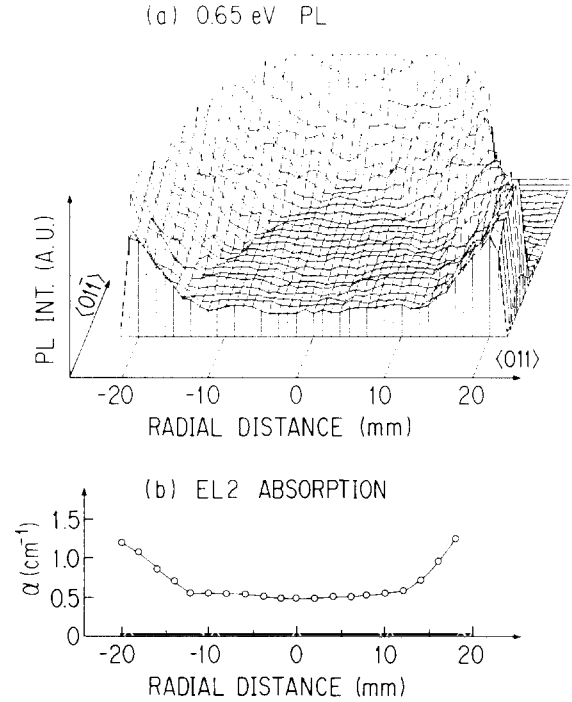


Fig. 3. Comparison of EL2 distribution between PL and optical absorption analyses. (a) Pseudo three-dimensional plot of the 0.65 eV band on half of an undoped SI LEC GaAs (100) wafer, with a cross section parallel to the $\langle 011 \rangle$ direction. (b) Profile of optical absorption coefficient of $1.1 \mu\text{m}$ across a wafer diameter corresponding to the cross section of (a) [7].

A typical example of the mapping of the 0.65 eV band on half of a (100) wafer is shown in fig. 3a [7]. The beam diameter of the excitation laser was 1 mm and the data point interval was 1 mm. A U-shaped intensity profile was observed across the wafer diameter with the characteristic four-fold symmetry of the (100) wafer. The optical absorption coefficient of $1.1 \mu\text{m}$, commonly used as a measure of the EL2 concentration [12], was measured on an adjacent wafer with a thickness of 4 mm. The distribution of the absorption coefficient of $1.1 \mu\text{m}$ across a wafer diameter, corresponding to the cross section of fig. 3a, is shown in fig. 3b. There is a close agreement between the two profiles.

A semi-quantitative relationship between the PL intensity and the EL2 absorption is generally recognized for randomly selected wafers under identical experimental conditions, as shown in fig.

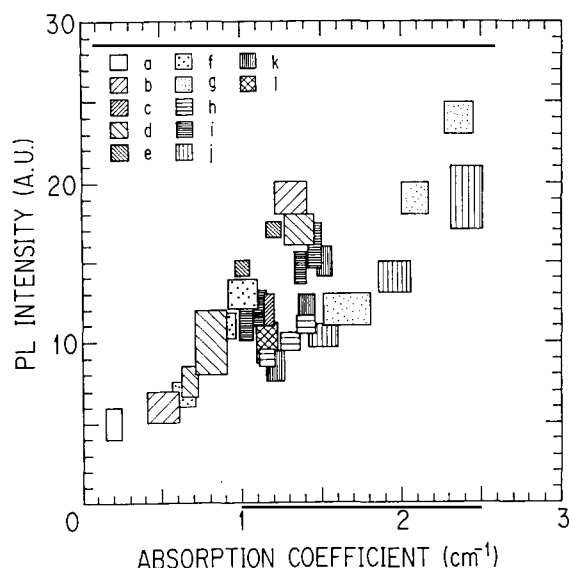


Fig. 4. Correlation between the PL intensity of the 0.65 eV band and the $1.1 \mu\text{m}$ absorption coefficient for a wide variety of undoped SI LEC GaAs wafers [7].

4 [7]. In most samples, the data points fall on a straight line which intercepts the origin. The deviation comes from the difference in the charge state of the EL2 level among the samples, the inhomogeneity of the sample between the PL and absorption analyses, and the difference in the surface finish among the PL samples.

It should be noted that the intensity of the band-to-band emission differs more than one order of magnitude, depending on the sample and on the surface treatment. In contrast, the EL2-related band is in the similar intensity range as shown in fig. 4, and the effect of the surface treatment is much less than that for the band-to-band emission. This fact cannot be explained by the simplified model (eqs. (1) and (2)), and further investigation will be required to clarify this point.

4.2. Thermal donor in Si

Heat-treatment around 450°C produces so-called “thermal donors” (TDs) in Si crystals containing oxygen [13]. Analysis of TDs is very important, because their formation distorts the expected resistivity, and because understanding of the microscopic origin of the TDs leads to a

clarification of the oxygen precipitation mechanism.

Photoluminescence spectroscopy has been used to detect the TD-related lines. The 1.143 eV band (the TD band) [14] and the 0.767 eV line (P line) [6,15,16], observed at low temperatures, were shown to be associated with the TDs. In order to detect the TD-related signal at room temperature, the temperature dependence of the PL spectrum was investigated. The 1.143 eV band was observed only at liquid helium temperature. The 0.767 eV line was always accompanied by a broad band around 0.7 eV. This 0.7 eV band was observable at room temperature, although the 0.767 eV line disappeared at temperatures higher than 150 K.

The PL spectra of a Czochralski (CZ) grown Si wafer before and after annealing at 470°C for 64 h are shown in fig. 5, where the excitation intensity is 0.4 W cm^{-2} . The 0.7 eV band appeared only when the sample was annealed around 450°C . The 1.1 eV and 0.7 eV bands are due to the band-to-band and trap-related transitions, re-

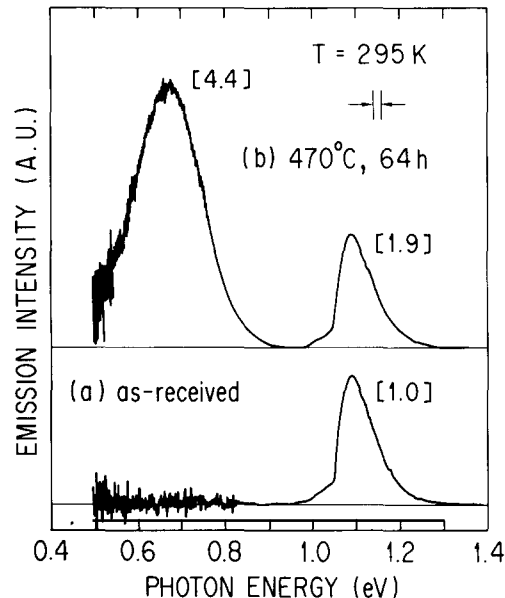


Fig. 5. PL spectra at room temperature of CZ Si crystal (a) before and (b) after annealing at 470°C for 64 h, where the excitation intensity is 0.4 W cm^{-2} . The spectral response of the measurement system is calibrated with blackbody radiation. The abscissa and the ordinate are proportional to the photon energy and the number of photons, respectively.

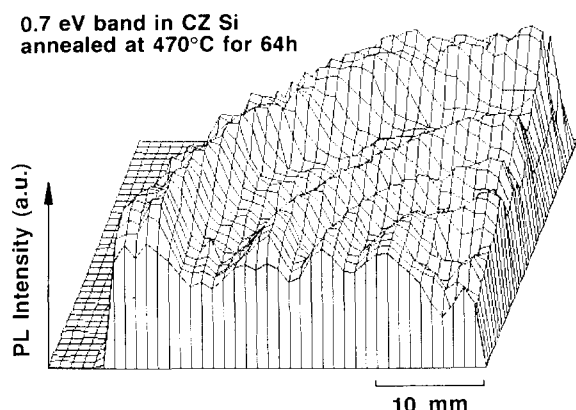


Fig. 6. Pseudo three-dimensional plot of the 0.7 eV band on a quarter of a CZ Si wafer annealed at 470°C for 64 h.

spectively, from the super-linear and linear relationships between the PL and excitation intensities. Mapping of the 0.7 eV band on a quarter of the wafer is shown in fig. 6, where both laser beam size and data point interval are 1 mm. A characteristic growth-striation pattern was observed. The intensity variation of the 1.1 eV band was rather flat on the wafer. It should be noted that the similar striation pattern was observed in the resistivity variation, but not in the distribution of the oxygen concentration. The present result suggests that some nuclei, distributed along the growth striation, play an important role in the oxygen agglomeration responsible for the TD-related defect.

5. Summary and conclusion

The room-temperature PL mapping technique has been used to characterize deep levels associated with microdefects in semiconductor wafers. A weak excitation condition, high stability of the measurement system, and appropriate surface finish of the sample are key points for the achievement of an accurate analysis. Two typical examples of deep-level mapping are presented: the EL2 level in GaAs and the TD in Si. The 0.65 eV band, always observed in undoped SI GaAs crystals, is due to the EL2 level. Mapping of the 0.65 eV band on various wafers indicates a high degree of

correlation with the EL2 absorption. This enables us to perform a semi-quantitative mapping of the EL2 level by the technique. The 0.7 eV band, appearing in CZ Si wafers annealed around 450°C, is considered to be due to the deep level associated with the TDs. A distinct growth-striation pattern is observed on a wafer, corresponding to the resistivity variation.

The deep-level PL mapping at room temperature has great practical advantages. The technique enables us to perform the semi-quantitative characterization of the deep-level defects in an as-received commercial wafer. Neither the preparation of a wafer polished on both sides as in the optical absorption method [17], the sample cooling as in the low-temperature PL method [5], nor the high vacuum as in the cathodoluminescence method [18] is necessary. The present technique makes it possible to characterize the deep-level distribution in the surface region, used as a device-active layer, with a high spatial resolution. This type of characterization of the deep levels has never been realized by any of the methods reported previously.

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