Ultraviolet anti-Stokes photoluminescence in GaN single crystals

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Abstract
Ultraviolet anti-Stokes photoluminescence (ASPL) is observed under continuous visible light excitation in a GaN single crystal at 4 and 77 K. The ASPL spectra are almost the same as the Stokes photoluminescence (SPL) spectra under band-to-band excitation. Namely, we observe ASPL due to bound and free excitons at 4 and 77 K, respectively. Based on the temporal decay, the excitation spectrum and the excitation intensity dependence of the ASPL intensity, we propose a two-step two-photon absorption mechanism through an electron trapped at a deep ionized donor with a lifetime of 1.45 ms.

1. Introduction

Many extensive studies have been performed on anti-Stokes photoluminescence (ASPL) in bulk semiconductors [1–3], quantum-well structures [4, 5], hetrojunctions [6] and nanocrystals [7, 8]. ASPL has been interpreted as being due to a two-step two-photon absorption process [1–3, 5, 7, 8], a direct consequence of photon recycling [4], or an Auger fountain mechanism [6]. The ASPL in indirect type semiconductors GaP [2] and Cr doped ZnSe [3] appear even under excitation by a cw low-power laser. In these crystals only charged carriers are generated and visible ASPL is emitted, but no band edge ASPL due to excitonic transitions is observed.

On the other hand, ASPL under weak excitation is observed in the direct wide band gap semiconductor GaN for the first time as far as we are concerned. Bulk GaN is currently of great interest for use as electrically conductive, lattice- and thermal expansion coefficient-matched substrates for GaN epilayers. The observed ultraviolet (UV) ASPL is due to bound and free excitons at 4 and 77 K, respectively, which is different from the cases of GaP and ZnSe:Cr. The UV ASPL of GaN under excitation sufficiently below the band gap is compared with the Stokes photoluminescence (SPL) under excitation above the band gap, and we propose a two-step two-photon absorption process through a deep donor intermediate state with a long lifetime to interpret the ASPL.
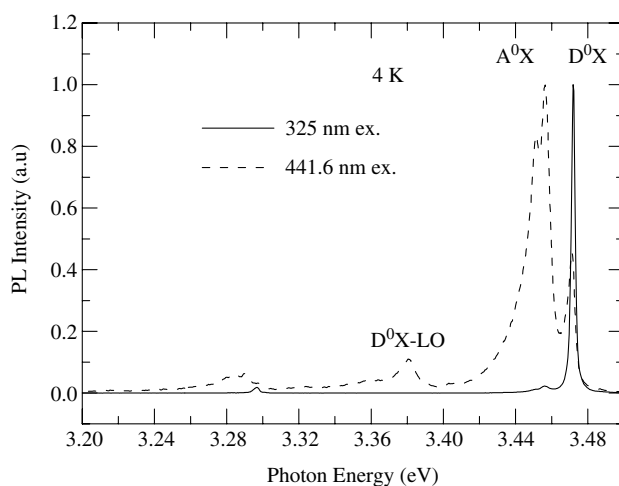
Figure 1. The solid and broken lines show the SPL and ASPL spectra under 325 and 441.6 nm excitations, respectively, at 4 K. A D^0X bound exciton line is observed at 3.471 eV, two A^0X bound exciton lines at 3.456 and 3.452 eV, and a D^0X LO line at 3.381 eV.

2. Experimental technique

The sample used was a single GaN crystal grown by Mitsubishi Chemical Co., using hydride vapour phase epitaxy (HVPE), with dimensions of $6 \times 5 \times 0.57$ mm^3. The crystal was attached to a copper sample holder of a cryogenic refrigerator using silver paste and cooled to 4 K. The sample temperature was measured using a silicon diode temperature sensor. The excitation light sources used were a He–Cd laser emitting at 441.6 and 325.0 nm at powers of 35 and 5 mW, respectively, and an Ar$^+$ laser emitting at 457.9, 476.5, 488.0, 496.5 and 514.5 nm lights, at a constant power of 35 mW. The laser light was focused on the cleaved surface (M plane) of the crystal, resulting in a power density of about 100 W cm^{-2} on the surface. The photoluminescence (PL) in the backwards direction was focused on the entrance slit of a monochromator with a reciprocal dispersion of 1.7 nm mm^{-1}. For typical SPL measurements, the 325 nm He–Cd laser light was used as the excitation source. For ASPL measurements, the 441.6 nm He–Cd laser light and above-mentioned Ar$^+$ laser lights were used as excitation sources, and a UV light pass filter (UVD-36B) was used on the PL side to avoid any scattered excitation light. The monochromatized light was detected using a Hamamatu Photonics multichannel analyser. The spectral resolution of the entire system was 0.7 nm.

For measuring time-resolved PL spectra, the 441.6 nm laser beam was pulsed using a mechanical light chopper. The obtained rectangular light pulse had a width of 5 ms, a repetition rate of 100 Hz and a decay time of 10 μs. The PL was focused on the entrance slit of a monochromator with a reciprocal dispersion of 22 nm mm^{-1} and detected using an integrated charge-coupled device camera (Princeton Instruments 576G) with a gate width of 4.7 μs. The measurement system for an electron lifetime in an intermediate state of a two-step absorption process will be described later.

3. Results and discussion

Figure 1 shows the PL spectra of the GaN crystal in the UV region at 4 K. The solid and broken curves show the PL spectra for 325 and 441.6 nm excitations, respectively. The photon energy
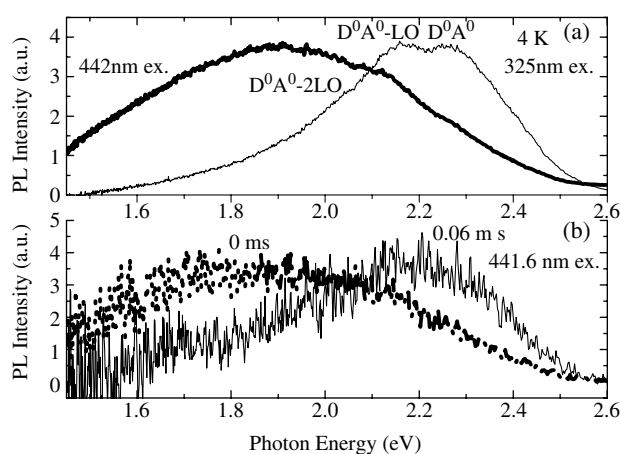
Figure 2. (a) The bold and fine lines show the time integrated SPL spectra for 441.6 and 325 nm excitations, respectively, at 4 K. Zero, one, and two LO phonon bands due to donor–acceptor pair recombination are observed at 2.26, 2.16 and 2.05 eV, respectively. (b) The bold and fine lines show SPL spectra under 441.6 nm excitation and at 0.06 ms after a 441.6 nm light pulse, respectively, at 4 K.

of the 325 nm light (3.81 eV) is larger than the exciton formation energy (3.48 eV), while that of the 441.6 nm light (2.81 eV) is much smaller. Hence, the former and latter curves show the SPL and ASPL spectra, respectively. In the SPL spectrum, a very distinct narrow line due to an exciton bound to a neutral donor (D^0X) appears at 3.471 eV, and two indistinct narrow lines due to an exciton bound to a neutral acceptor (A^0X) appear at 3.455 and 3.450 eV [9]. On the other hand, in the ASPL spectrum, the D^0X and A^0X lines appear, but the peak position of the D^0X line is slightly shifted to the lower energy side and the D^0X intensity is only half of the A^0X intensity. The peak shift and weaker intensity of the D^0X ASPL may be caused by the reabsorption of the PL, because most of the 441.6 nm light passes through the crystal. Namely, the PL is emitted on the path of the excitation light, but only the PL near the surface can exit the crystal without being reabsorbed. In this energy region, the Urbach tail of the intrinsic absorption is considered to exist. Unfortunately, as the crystal used is too thick, the absorption coefficient in this energy region could not be measured. If the Urbach tail overlaps with the bound exciton absorption line, the absorption coefficient at the energy of the D^0X line may be larger than that of the A^0X line. As a result, the D^0X PL may be more strongly reabsorbed than the A^0X PL. Even within the D^0X line, the degree of reabsorption increases with increasing the photon energy, which results in the red shift of the D^0X line. Accordingly, it is considered that the ASPL spectrum is essentially the same as the SPL one. This is different from the cases of GaP [2] and ZnSe:Cr [3], where no excitonic PL is observed. The ASPL intensity remains constant even after a long irradiation of the 442 nm laser light, which is one of the characteristic phenomena. From these results, it is considered that a free electron–hole pair or a free exciton is generated by a two-step two-photon absorption process through an intermediate state with a long lifetime having an energy within the band gap. That is then bound to a donor or an acceptor. The detailed mechanism is stated later.

To study the generation mechanism of the ASPL, the PL spectrum on the Stokes side under 441.6 nm excitation (bold line) is shown in the upper part of figure 2 together with that under 325 nm excitation (fine line). A broad band at 2.28 eV and the LO phonon side bands under the 325 nm excitation are due to the so-called yellow PL, which is considered to
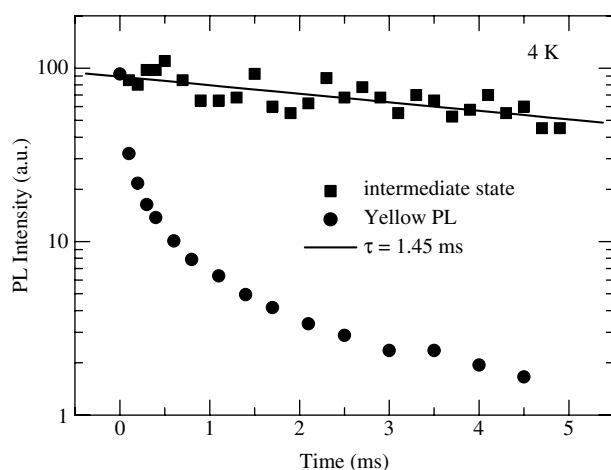
Figure 3. The decay profile of the electrons in the intermediate state of the two-step absorption process and that of the yellow PL intensity at 4 K are shown by squares and circles, respectively, on a semi-logarithmic scale. The straight line represents a decay time of $\tau = 1.45$ ms.

be associated with a donor–acceptor pair (DAP) recombination [10, 11]. On the other hand, under 441.6 nm excitation, a broad band mainly appears at 1.9 eV (red PL) in addition to the weak yellow PL band. The most plausible reason for the large difference observed in the PL spectra is as follows. The entire region of the bulk crystal is excited under the 441.6 nm irradiation, while only the surface of the crystal is excited under the 325 nm irradiation. This is because the penetration depth of the 325 nm light is only 8×10^{-6} cm [12]. The crystal surface may be mechanically damaged or oxidized, and hence, the ionized donor and/or acceptor concentrations may be high on the surface. As a result, the yellow PL due to the DAP may be observed. In contrast, these concentrations are insufficiently high inside the crystal, and hence, some of the electrons and/or holes are not trapped at the ionized donors and/or acceptors, but at deep impurity centres. The trapped carriers at the deep impurity centres may emit the red PL. Namely, we may be able to know the optical properties of the bulk from the ASPL spectrum.

In the lower part of this figure, time-resolved spectra under the 441.6 nm light excitation are shown. The PL spectrum under the 441.6 nm light excitation and that at 0.06 ms after a rectangular excitation light pulse are shown by bold and fine lines, respectively, where the peak intensities are normalized. The former and latter spectra are similar to the ASPL and SPL spectra, respectively. Accordingly, we can conclude that the red PL rapidly decays within 0.06 ms and that the yellow PL has a decay time longer than 0.06 ms.

Figure 3 shows the decay profile of the yellow PL intensity (closed circles) under 441.6 nm light excitation and of the electron density in the intermediate state (closed squares) on a semi-logarithmic scale. The latter was obtained from the time decay of the ASPL intensity by the following method. As the ASPL spectrum does not depend on the time, the ASPL intensity of the A^0X bound exciton was monitored. The 441.6 nm laser beam was divided into two beams using a half mirror. One of them was focused on the sample after being chopped and the other was focused on the same point without being chopped. The detection system was the same as that for the time-resolved PL spectra. Here, we assume that the ASPL intensity is proportional to the electron density in the intermediate state. This assumption is reasonable, because free or bound excitons are formed using the 441.6 nm light with lifetimes ($<$100 ps [13]) that are extremely short compared to that of the electron in the intermediate state (1.45 ms) as will be
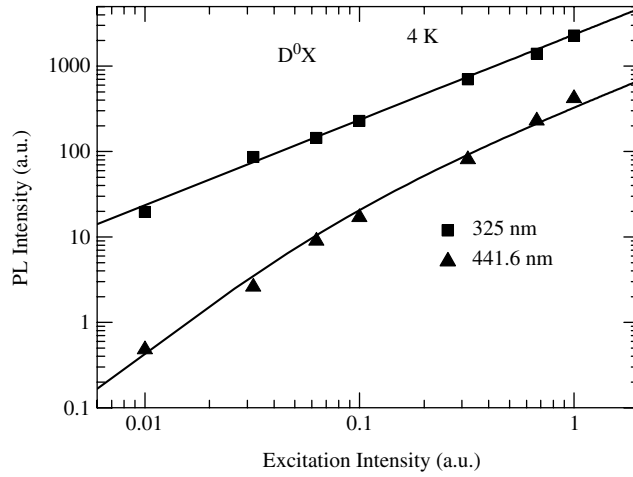
Figure 4. The excitation intensity dependences of the D^0X intensity under 325 and 441.6 nm excitation are shown by squares and triangles, respectively. The straight line represents a power of 1.0 under 325 nm excitation at 4 K. The solid curve represents equation (3) with an adjustable parameter, $\tau_2/\tau_1 = 0.07$.

shown later. The lifetimes of free and bound excitons are also confirmed by the decay time of the ASPL of less than 10 μs in this work, which is still shorter than that of the electron lifetime in the intermediate state. When the pulsed light is not irradiated, the ASPL appears not only by the two-step absorption of the continuous light, but also by the absorption of the continuous light from the remaining electrons in the intermediate state generated by the previous pulsed light. If the ASPL intensity due to only the continuous light is subtracted from the observed ASPL intensity, then the time decay of the subtracted ASPL intensity represents the temporal decay of the electron density in the intermediate state. Thus the lifetime of the electron in the intermediate state can be obtained by this method. The straight line in figure 3 represents the lifetime ($\tau = 1.45$ ms) of electrons in the intermediate state. On the other hand, the yellow PL intensity shows a non-exponential decay, which is characteristic of the donor–acceptor pair recombination [14]. This decay profile is quite different from that of the electrons in the intermediate state of the two-step absorption process. Accordingly, the intermediate state is not the DAP associated with the yellow PL. From this result, however, we cannot know whether the donor state associated with the intermediate state is in common with that of the DAP or not.

To study the two-step absorption process, we measure the excitation light intensity dependence of the ASPL. Figure 4 shows the excitation intensity dependences of the D^0X PL intensity under 441.6 and 325 nm excitation as denoted by triangles and squares, respectively, on a logarithmic scale. The A^0X SPL and ASPL intensities show the same excitation intensity dependence, although it is not shown here. The straight line represents the linear relation between the SPL and excitation intensity. This linear relation indicates that the D_0X and A_0X densities are proportional to the incident photon number.

On the other hand, the excitation intensity dependence of the ASPL is explained by the following rate equations.

$$\mathrm{d}m/\mathrm{d}t = L - m/\tau_1 - mL/\tau_2 = 0 \tag{1}$$

$$\mathrm{d}n/\mathrm{d}t = mL/\tau_2 - n/\tau_3 = 0, \tag{2}$$

where m and n are the electron densities for the two-step absorption process in the intermediate
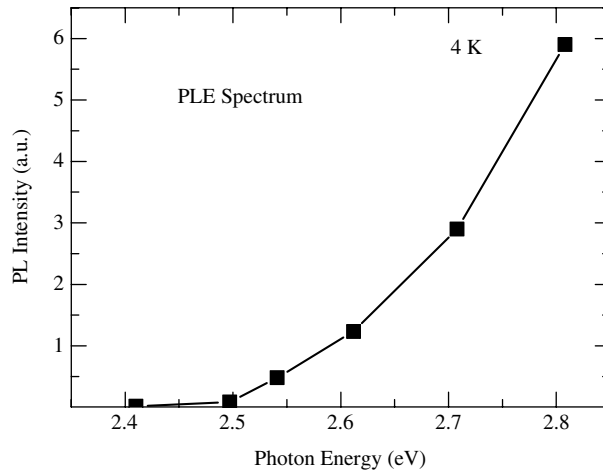
Figure 5. PLE spectrum for the ASPL at 4 K. The A^0X PL is detected.

and final states, respectively. The other symbols are as follows: L is the absorbed photon density; $1/\tau_1$ is the recombination rate of electrons in an intermediate state; $1/\tau_2$ is the two-step absorption rate; and $1/\tau_3$ is the recombination rate of electrons in a final state.

In the steady state, the solution

$$n = \tau_3 L^2/(L + \tau_2/\tau_1) \qquad (3)$$

is obtained. If the excitation light intensity is proportional to L, and the PL intensity to n, equation (3) is fitted to the experimental points in figure 4. The solid line represents equation (3) with an adjustable parameter, $\tau_2/\tau_1 = 0.07$. This value indicates that most of electrons in the intermediate state are re-excited by the photon absorption.

Figure 5 shows the photoluminescence excitation (PLE) spectrum of the ASPL at 4 K. The shape of the ASPL spectrum is independent of the excitation energy. The PL intensity increases with increasing photon energy, and no peak is observed. This indicates that the initial or final state of the two-step absorption process is not a discrete state.

On the basis of these experimental results, we propose a two-step two-photon absorption process. On the basis of the energy conservation law, a two-step excitation process through a deep level is considered to be plausible. From the long lifetime, 1.45 ms, of the electrons in the intermediate state it is suggested that a deep level contributes to the two-step absorption process, because the electron state in the deep trap is considered to be mixed with the triplet state. In general, a photo-excited electron in a deep trap is relaxed to a lower energy level following lattice distortion [15]. Hence, we will discuss the two-step absorption process using a one-dimensional configuration coordinate model, as shown in figure 6. The abscissa represents a configuration coordinate, i.e., a displacement of surrounding lattices in a deep trap from the equilibrium position. The ordinate represents adiabatic potential energy. The energy of the electron is measured from the top of the valence band in the undistorted lattice. The hatched areas represent many parabolic curves which distinguish the dispersion of the electron and hole band in the rigid lattice. The p-like valence electron is excited to an ionized donor states (an electron in a deep trap) by the first photon absorption process. As the valence electron has a kinetic energy, the transition energy has a finite width, although the transition probability is small. If an electric dipole transition occurs, the wavefunction of the photo-generated electron should be s-like. After the lattice relaxation, the electron in the surrounding
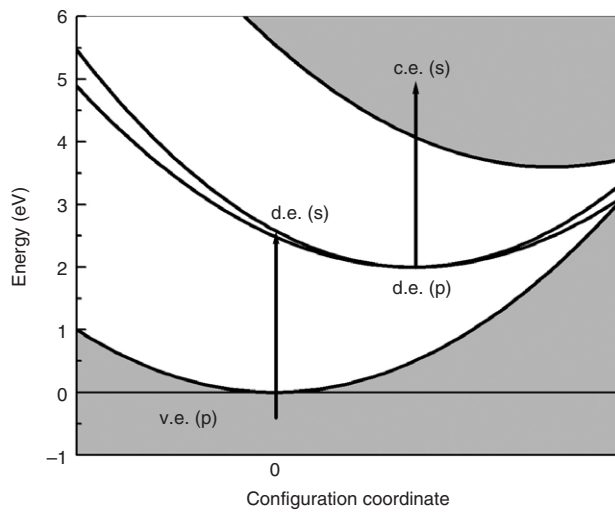
Figure 6. One-dimensional configuration coordinate diagram. The abscissa and ordinate represent the configuration coordinate and adiabatic potential energy, respectively. The uppermost and lowest curves represent the bottom level of the conduction band and the top level of the valence band, respectively. The intermediate curves represent the energies of an electron trapped at an ionized deep donor. Symbols in parentheses represent electron symmetry. The electric dipole transitions are indicated by arrows.

displaced lattices may have p-like character, which is caused by Jahn–Teller interactions. In general, the wavefunction of the relaxed p-like electron in the deep trap contains a triplet wavefunction, resulting in the small radiative transition probability. Therefore, most of the relaxed p-like electrons may be ionized to the s-like conduction band by the second photon absorption process. As a result, free electron–hole pairs are formed and then they recombine to form excitons. As the relaxed electron in the deep trap has a long lifetime, the two-step absorption process predominantly occurs even under the continuous light excitation. No peak in the PLE spectrum of figure 5 is considered to be originated from the kinetic energies of the conduction and valence electron. In this proposed mechanism, the presence of a deep ionized donor is essential. Unfortunately, the slight absorption associated with the deep donor was not directly observed because of Rayleigh and Mie scatterings.

At 77 K, the bound excitons and the DAP are unstable, and the free exciton PL is strongly observed in the usual SPL spectrum. Thus, the process of the ASPL can be discussed under the situation where the shallow donors and acceptors are thermally unstable. The solid and dashed lines in figure 7 show the PL spectra under the 325 and 441.6 nm light excitations, respectively. The lines at 3.47 and 3.45 eV under the 325 and 441.6 nm excitation, respectively, are associated with the free exciton recombination [16]. The red shift of the zero phonon line under 441.6 nm excitation is due to the reabsorption of the emitted light. The lines at 3.39 and 3.30 eV indicate one and two LO phonon side bands, respectively. The excitation intensity dependences of free exciton PL intensities for 325 and 441.6 nm excitations are shown by squares and circles, respectively, in figure 8. At 77 K, the linear dependence is also observed for the SPL. The excitation intensity dependence of the ASPL is compared with equation (3). The lower solid curve represents equation (3) with an adjustable parameter $\tau_2/\tau_1 = 0.05$. This small value indicates that the two-step two-photon absorption process is dominant also at 77 K.
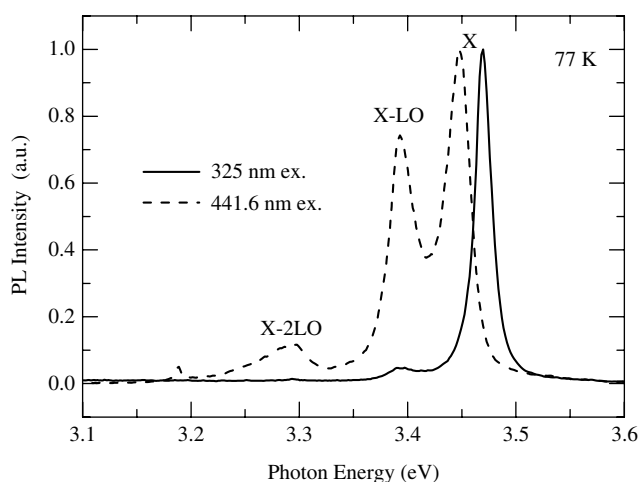
Figure 7. The SPL and ASPL spectra under 325 and 441.6 nm excitation at 77 K are shown by
the solid and broken lines, respectively. Zero, one and two LO phonon side bands of a free exciton
PL are observed at 3.470, 3.393 and 3.295 eV, respectively, in the SPL and ASPL spectra. The
zero phonon line in the ASPL spectrum appears at 3.448 eV, which is red-shifted by a reabsorption
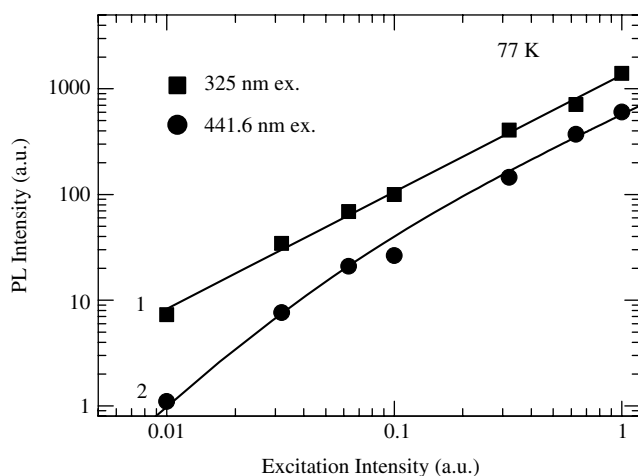effect.

Figure 8. The excitation intensity dependences of the free exciton PL intensity under 325 and
441.6 nm light excitation at 77 K are shown by squares and circles, respectively. The solid curve
represents equation (3) with an adjustable parameter $\tau_2/\tau_1 = 0.05$.

In summary, we found ultraviolet ASPL under visible light excitations in a single GaN
crystal at 4 and 77 K. From the excitation intensity dependences of the ASPL intensity, the
lifetime measurement of the intermediate state electron for the two-step absorption process,
and the excitation spectrum of the ASPL, we propose a mechanism consisting of a two-step
two-photon absorption process through an intermediate state of a deep ionized donor having
energy within the band gap.

Acknowledgments

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