Temperature-dependent linewidth of single InP/$Ga_xIn_{1-x}P$ quantum dots: Interaction with surrounding charge configurations

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We have investigated individual metal-organic vapor phase epitaxy-grown self-assembled InP quantum-dots in a $Ga_{0.5}In_{0.5}P$ matrix by means of photoluminescence with high spatial resolution as a function of temperature and excitation density. We observe an abrupt change from the well-known but yet unclear relatively broad emission band at low temperatures to narrow lines at $T \geqslant 45$ K. The high-temperature mode is the one expected for a fully confined quantum system. The ubiquitous broadening at low temperature is discussed in the framework of spectral diffusion, i.e., fluctuating charge configurations surrounding the quantum dot influence its transition energies. We conclude that the interacting charges are most probably trapped in connection with thickness variation in the wetting layer. Their release at higher temperatures removes the perturbation and leads to the expected appearance of sharp single dot spectra.

I. INTRODUCTION

Within the great variety of quantum dot (QD) systems fabricated by different techniques[1] self-assembled dots (SAD) grown in the so-called Stranski-Krastanov (SK) mode are of considerable interest.[2–6] Because of their dislocation-free, nm-size geometry and relatively good size homogeneity they offer great potential not only for studying basic properties, but also because of possible applications like data storage[7] and solid state-lasers.[8]

In recent years optical investigations for studying QD's have been improved towards high spatial resolution close to the diffraction limit and beyond. This allows for *single dot spectroscopy*,[9–23] which suppresses the inhomogeneous broadening inevitably present if the experiment averages over an ensemble of size distributed QD's. With the improved optical access the ground-state transition of single InP SAD embedded in a $Ga_{0.5}In_{0.5}P$ matrix turned out to have a relatively large photoluminescence (PL) linewidth of several meV at low temperatures.[10,11] This is in striking contrast to the expected δ function like density of states and hence sharp transition lines of a quantum-mechanical particle in a box. Even more sophisticated theoretical calculations of the optical spectra of the system under investigation[24] gave no explanation for this behavior up to now.

In this paper we demonstrate temperature and excitation intensity dependent single dot spectroscopy of an InP SAD system by means of micro-PL (μPL). The temperature and excitation intensity turn out to have a great influence on the unexpected linewidth behavior. By increasing the temperature the emission spectrum *switches* abruptly to a *narrow* line emission mode, reflecting the typical features of a single QD spectrum at $T \geqslant 45$ K.

By means of its linewidth the QD probes the surrounding charge configurations, which are in turn controlled by the temperature-dependent Fermi level.

II. EXPERIMENT

The samples investigated were grown by metal-organic vapor phase epitaxy (MOVPE) on (100) GaAs substrates with 2° misorientation towards (110). After a GaAs buffer layer of 250 nm a 500-nm $Ga_{0.5}In_{0.5}P$ [(GaIn)P hereafter] layer was grown. The InP QD's developed from an InP sheet of nominally 1.6 monolayers (ML's) during a growth interruption of 4 s. These were capped with another 200 nm of (GaIn)P. The growth temperature was 580 °C. For more details see Ref. 25.

The topography of the InP deposition was studied by atomic force microscopy on a reference sample grown under the same conditions, but without (GaIn)P capping layer. These measurements in connection with more detailed investigation of InP epitaxial growth[26] lead to the following description of the structure: SAD's with a geometry of truncated pyramids with $\approx$18-nm height and $\approx$35-nm base length dominate the spectra. The density of the dots is less than one per μm^2. In addition partially formed islands are observed, thoroughly investigated by other groups and reflecting the so-called bimodal growth.[6,25] Finally a wetting layer (WL) of 1–4 ML's is expected between the larger objects providing a quantum well (QW) of varying thickness, and able to trap free charges.

The μPL measurements with spatial resolution of less than 500 nm were made with a reflector based objective within a confocal setup.[27] The sample—directly mounted on the back face plate of the objective—was placed in a gas flow cryostat for temperature variation in the range of 3–100 K. This setup enables us to investigate single InP QD's without a patterning of the sample, and easy access to excitation intensity over three orders of magnitude is also possible. We dispersed the PL signal with a 0.6-m monochromator and detected it with a liquid-nitrogen-cooled charge-coupled device camera. The spectral resolution of the setup was 200 μeV. Excitation was done by an Ar^+ laser at 2.41 eV.

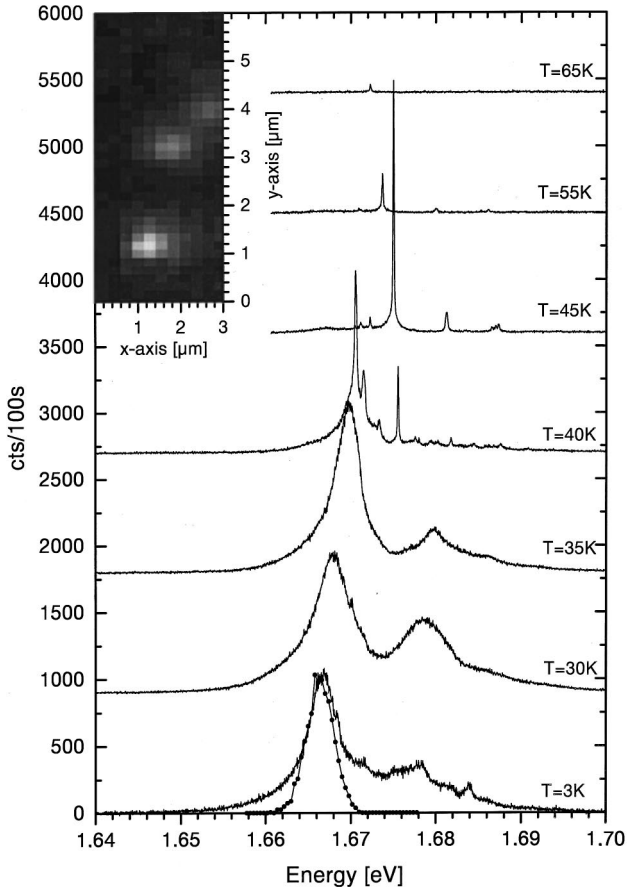

FIG. 1. Temperature series of single dot photoluminescence spectra. Note the abrupt charge of the linewidth when going from 35 to 45 K. The dotted curve gives the result of the model calculation for point charges. In the inset a $6\times3\mu$ m^2 luminescence map is shown. The emission was collected from the energy interval 1.61–1.68 eV.

III. RESULTS AND DISCUSSION

Figure 1 is a series of typical μPL spectra of a single SAD at different temperatures. The inset shows a two-dimensional luminescence map (detection energy 1.61–1.68 eV) of a 6×3-μm^2 area and demonstrates the ability of probing a single QD. All spectra were checked to be definitely from isolated QD's.

The spectrum recorded at $T=3$ K has a pronounced lowest energy transition centered at 1.667 eV with the broad linewidth of 4.6 meV. There are also transitions at higher energies, which were investigated carefully by Hessman *et al.*[11] and shall not be subject of this paper. The change of the spectra for increasing temperatures up to 35 K is moderate. Besides a significant blue-shift the integral intensity increases. Further raising the temperature leads to abrupt changes in the luminescence spectra. Within $\Delta T=5$ K the broad emission band switches into an intermediate mode of several lines ($T=40$ K), and then to a single sharp peak of linewidth <200 μeV ($T=45$ K and higher). This peak has an energy located above the upper half point of the low-temperature broad emission band. Temperature series for many different QD's showed in most cases the same qualitative behavior. In some rare cases though the linewidth decreased less or the switching did not occur in the temperature range investigated. The moving of the sharp peak to lower energies with increasing temperature is consistent with a temperature related band-gap shift of InP $\Delta E=0.58$ meV/K.[28]

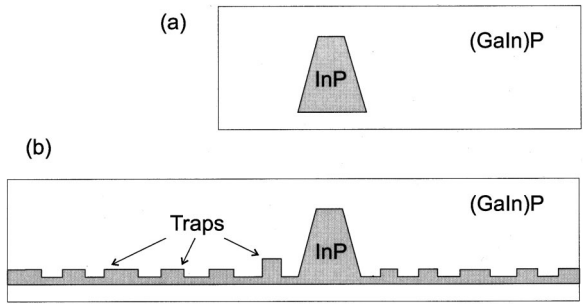

FIG. 2. Sketch of the InP Stranski-Krastanov layer in the (GaIn)P matrix: (a) idealized as in the calculation of Ref. 24, (b) more realistic including the wetting layer or other surrounding perturbations.

The upper limit for the excitation rate of carriers in this measurement is $\approx4\times10^9$ s^{-1} in the probed volume (excitation density 0.835 W/cm^2). The stationary number of electron-hole pairs in the dot is determined by the lifetime of <1 ns (Ref. 11) and competing relaxation mechanisms. Taking this into account, the electron-hole occupation of the SAD itself should be less than 1.

We discuss four major points to explain the experimental findings: (i) The most pronounced sharp line in the high-temperature spectra represents the unperturbed transition from the lowest-lying excitation state of the QD. (ii) The broadening of this emission line at low temperatures is induced through interaction of the QD electron and hole states with charges being trapped or released by surrounding sites, leading to a fluctuating charge configuration. (iii) The mode of the QD luminescence (being broad band or narrow line) depends on the position of the Fermi level controlling the charging of the sites. (iv) The Fermi level is determined by the n doping of the barrier material and the temperature.

The narrow and temperature independent emission linewidths in the high-temperature spectra reflect what one would expect from a confinement in all three spatial dimensions, i.e., the δ-function-like density of states. We therefore denote this appearance as the unperturbed case, which can be well compared with the very detailed theoretical study of the luminescence of InP dots in a (GaIn)P matrix performed by Pryor, Pistol, and Samuelson.[24] In Fig. 2(a) we give a two-dimensional sketch of the geometry of the InP dot underlying these calculations. Taking the mean size of our truncated pyramids into account the lowest-lying transition energies for theory and experiment provide acceptable agreement. Furthermore, the calculations suggest the measured peak at 1.6815 eV to be the next excited state because the energy offset with respect to the forementioned energy is of the same order of magnitude as the calculated one. Note that Pryor's calculations assume a homogeneous idealized (GaIn)P matrix for the InP dots and do not reveal processes to explain the rather large linewidth in the low-temperature spectra.

We believe that the reason for the large linewidth is to be found in spectral diffusion due to electric fields connected to structural features surrounding the dot. This interpretation is

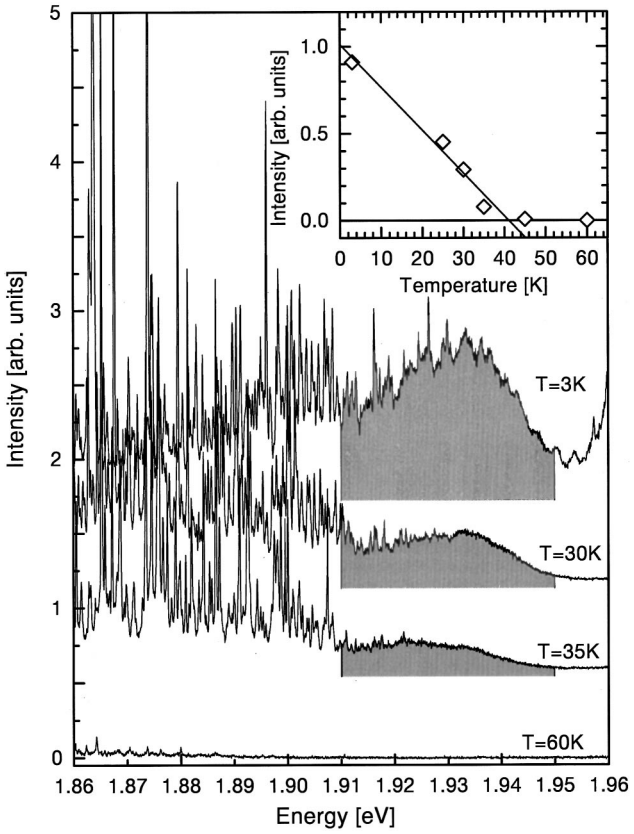

FIG. 3. μ-photoluminescence spectra of the wetting layer for various temperatures. Shaded areas reflect the limits for integration. Inset: dependence of the integral emission intensity (1.91–1.95 eV) on temperature.

closely related to the explanation of persistant spectral hole burning[29] and of the line broadening in CdSe single dot spectroscopy.[23] In the latter reference the line broadening is assumed to be due to variable electric fields resulting from carriers in the dot matrix and leading in turn to a variable quantum confined stark effect of the dot.

Most QD's in a semiconducting matrix though do not show broad lines as far as they are investigated by single dot spectroscopy at low temperature.[14–22] This supports the idea that the broad emission band is caused by a special configuration of the surrounding material. An interesting observation in this context has recently been made by Pistol *et al.* who found random telegraph noise in the PL of one out of a thousand SAD.[30] According to them, the switching on a seconds time scale is induced through defects in the vicinity of the dot.

The most obvious deviation of the idealized matrix is the WL inevitably connected with Stranski-Krastanov growth. Thickness variations in this layer from one to four ML's have been observed by means of PL. We believe these effective traps to be the sites mentioned in (ii). Therefore we performed temperature-dependent luminescence measurements of the respective energy interval, as presented in Fig. 3. In calculations of InP-QW's sandwiched in (GaIn)P for 1 and 2 ML's the energy shift relative to the barrier was found to be 14 and 47 meV, respectively.[6] Therefore the bandlike luminescence centered around 1.93 eV, i.e., 35 meV below the (GaIn)P bulk luminescence band, can be attributed to localizations esulting from clusters of 2-ML thickness with varying *lateral* confinement. The high spatial resolution allows us on the one hand to resolve some structure in the luminescence band, on the other hand the spatial density of the states is too high to resolve single localizations, as can be done in the low-energy part from 1.91 eV down to 1.82 eV (the latter limit not shown here). The carriers involved in this low-energy PL experience a weaker confinement, belonging to larger InP clusters. Returning to the temperature dependence of the WL luminescence around 1.93 eV a strong quenching of the intensity with increasing temperature can be observed. In the inset of Fig. 3 this dependency of the integral luminescence intensity ($\Delta E = 1.91$–1.95 eV) is displayed. The 3-K value was normalized. The temperature dependence is linear in temperature leading to complete suppression of WL luminescence at ≈ 40 K. This temperature corresponds to the one determined for the switch between the two occurrences in the single SAD spectra, consolidating the idea of the influence of WL states on the SAD luminescence.

After discussing the origin of the broad low-temperature emission we now elucidate the temperature induced switch of the emission mode [compare (iii)]. Since a simple thermal ionization (Arrhenius-like) of the traps would smear the transition to the unperturbed case over a larger temperature range we conclude that the influence of the temperature on the occupation of the traps is caused by the change of the Fermi level E_{Fermi}. We assume E_{Fermi} to be determined by the barrier material alone, because of the small amount of WL states compared to the volume donor states of $\approx 10^{16}$ cm^{-3} in our *n*-doped material. For this parameter we calculated the temperature-dependent bulk Fermi level by neutrality condition.[31] For high temperatures it will lie below the traps' depth [$E_{\mathrm{Fermi}}(T = 45\ \mathrm{K}) = 1.910$ eV] leaving the sites unoccupied, whereas for low temperatures it will populate the traps [$E_{\mathrm{Fermi}}(T = 3\ \mathrm{K}) \approx 1.955$ eV, strongly depending on the donor binding energy] and cause a fluctuating occupation within a range of $k_B T$.

p-doped samples as, e.g., grown by molecular-beam epitaxy (MBE) having a Fermi level close to the valence band and therefore leaving the localization unoccupied reveal sharp lines of ≈ 200 μeV even for low temperatures.[13,32]

Summing up the facts we consider the following scenario (compare Fig. 4): the dot is seen as a probe for the surrounding charge configurations which are modified by the temperature-dependent Fermi level. The dominant interaction leading to the spectral diffusion in this picture is Coulombic, reminding to the case of pair band recombination (D°,A°) known from bulk semiconductors. Since the fluctuations in trapping and release and therefore the spectral diffusion are fast compared with the PL measurements with an integration time of several seconds, the spectra reflect the time average over the different configurations. For low excitation the Fermi level is exclusively determined by the majority carriers of the barrier material (i.e., electrons) and will not be effected by the injected carriers. Starting with high temperatures the Fermi level is lying well below the WL traps' energies. Thus the WL short-range potential wells surrounding the dot are not occupied, one observes an unperturbed QD transition with narrow linewidth [Fig. 4(a)]. Decreasing the temperature (compare 40 K spectrum in Fig. 1) raises the Fermi level, starting to occupy few, very deep

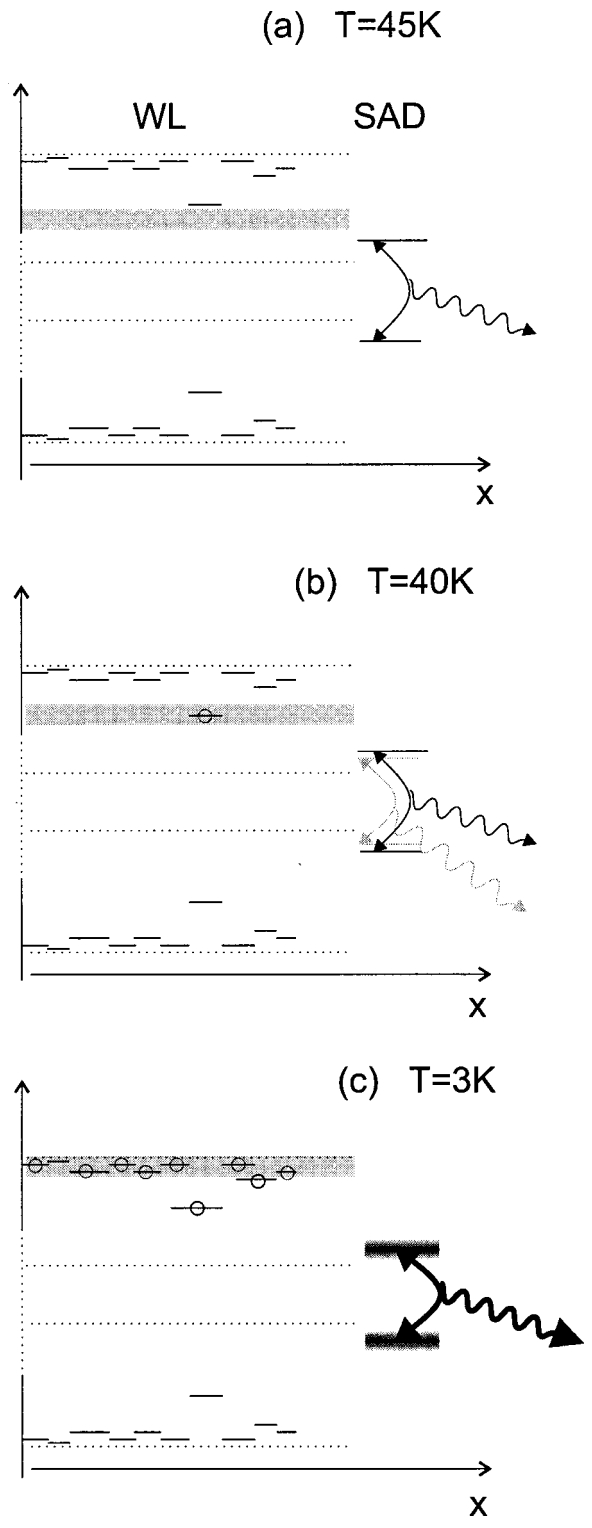

FIG. 4. Sketch of the temperature-dependent scenario of the dot luminescence: the shaded bar represents the softened region k_BT of the Fermi function. (a) Unoccupied states in the wetting layer (WL) lead to unperturbed photo luminescence of the self assembled dot (SAD) for high temperature. (b) Occupation of a low-lying trap due to the temperature induced increase of the Fermi level decreases the transition energy of the SAD. Both emission lines will be seen in photoluminescence because of the fluctuating occupation. (c) Fluctuating occupation of many traps leading to many different charge configurations and in turn a broad emission line.

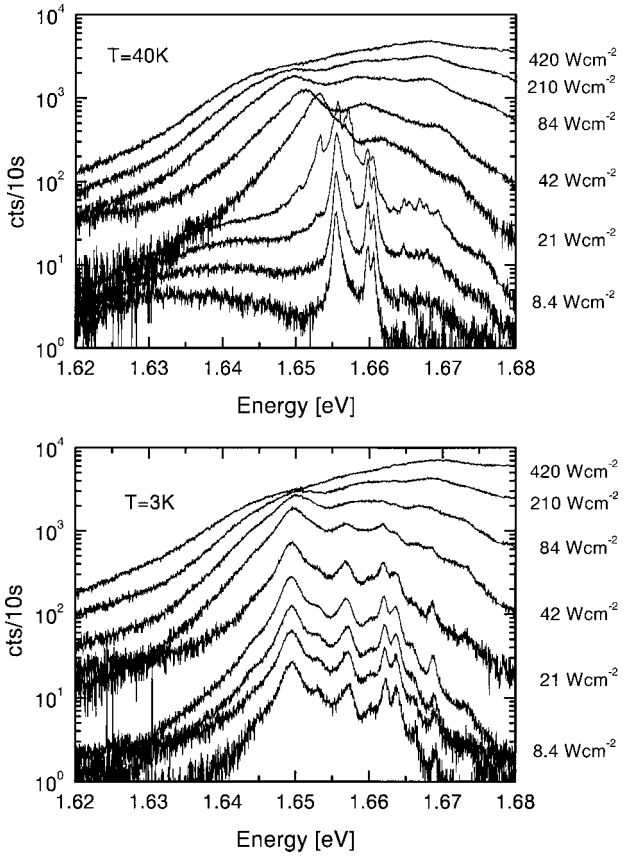

FIG. 5. Intensity series of single dot photoluminescence spectra for high (upper graph) and low (lower graph) temperatures.

localizations [in Fig. 4(b) only one is occupied for simplicity]. The occupied (i.e., charged) sites interact with the electron and hole states of the QD. The conduction-band wave functions are localized in the center of the dot. In contrast the valence-band wavefunctions are located at the core[24] leading to a dominant contribution of dot hole to WL-electron interaction and in turn a net energy lowering of the emission as observed in the spectra. Since the Fermi edge is broadened, those traps are not occupied constantly but their charge state fluctuates in time, leading to a variety [two in Fig. 4(b)] of WL-state configurations experienced by the QD. In the spectra sharp lines appear, each corresponding to one configuration. As the temperature is lowered further (below 40 K), the number of participating localizations will increase drastically, leading to the broad luminescence band [Fig. 4(c)]. The fast increase within 10 K is due to the small energy width of the Fermi edge ($k_BT \approx 3.4$ meV at $T=40$ K) compared with the total change of the Fermi level (15 meV for the interval of $T=35$–45 K). The width of the luminescence is now characterized by the broadening of the Fermi edge, the energetic distribution of the localizations determining the occupation, and the spatial distribution of the localizations near the QD determining the degree of interaction. Once the emission band is broad, further temperature decrease leads to an increase of involved charges, shifting the emission center to lower energies, as observed in the experiment.

Figure 5 shows a series of spectra with a variation of the excitation intensity over almost three orders of magnitude for $T=40$ K (upper graphs) and $T=3$ K (lower graphs). These measurements were performed on another dot showing quali-

tatively the same behavior, i.e., comparing the spectra at minimum excitation brings up broad linewidth for low temperature and small linewidth for high temperature. While the intensity dependence of the low temperature case seems to be negligible—except of the Pauli blocking effect for very high excitation—the sharp line in the 40-K spectra broadens significantly and shifts to lower energy with excitation increase until the spectrum finally is very similar to the corresponding spectrum ($42\ \mathrm{W/cm^2}$) for the low-temperature case. This intensity dependence is compatible with our model. If the excitation is increased above a certain level the description with one equilibrium Fermi level fails and two quasi-Fermi levels for electrons and holes, which are both determined by the injected carriers, have to be taken into account. $E^{(e)}_{\mathrm{Fermi}}$ will move upwards on increasing excitation power and overlap with the localizations. Therefore the WL trapping sites will be charged, regardless of the high temperature.

In a simple model we estimate the size of the fluctuating Coulomb interaction energy between the SAD electron and hole ground state and the surrounding electrons assumed to be point charges. For this model the following assumptions were made: (i) The polarization of the SAD was neglected. (ii) Occupation of the WL traps leads to an electron excess in the direct neighborhood of the SAD. The model calculation was performed as follows: The charge distribution of the SAD ground states was approximated by an electron charge at the origin and a ringlike positive charge around it (compare Fig. 6), taking into account the estimated diameter of the dot and summing up to one elementary charge. The trap sites were distributed binomially around the origin (small circles) within an area of radius smaller than 75 nm. The contribution of charges with larger distances can be neglected. Their corresponding localization depth was chosen to have a Gaussian distribution in energy space. According to the Fermi distribution with the Fermi edge at the center of Gauss function, the sites were occupied (circles with minus in Fig. 6) and the Coulomb terms reducing the QD-level energy were summed up for each individual configuration. 5000 configurations were averaged, leading to a distribution of emission lines. With a small broadening parameter to each line this simple model was able to reproduce the low-temperature spectra well (see Fig. 1, dotted curve), with reasonable parameters. Softening of the Fermi edge of $k_BT = 0.25$ meV corresponding to 3 K, the best fit required a distribution of 100 localizations with a minimum distance of 2 nm from the simulated dot's hole state surface to prevent divergences and a Gaussian distribution of energies with a width of 1 meV. The deviation of the dotted curve in Fig. 1 from the experimental spectrum as well as the unreasonable small energy distribution parameter of 1 meV is probably due to the neglect of polarizability or quantum-mechanical effects like wave-function overlap between SAD and trap states.

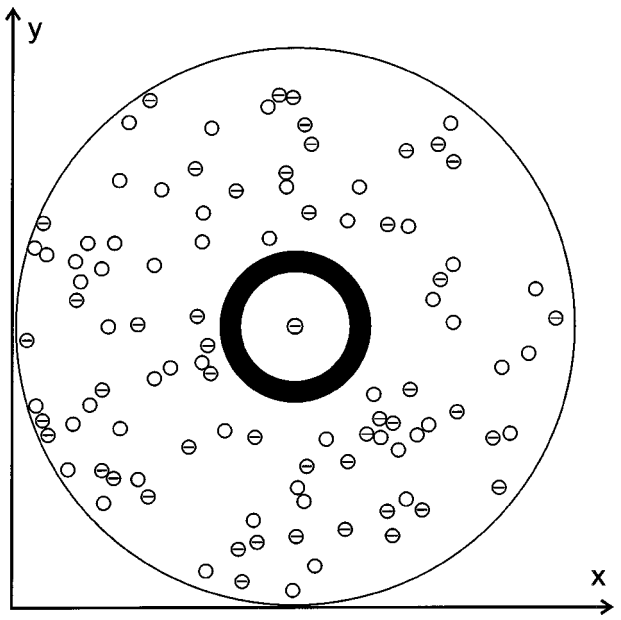

FIG. 6. Sketch of the charge distribution for the simulation. The circle at the origin and the black ring around it are the charges of the SAD electron and hole ground states, respectively. The small circles represent WL traps, which are partially occupied (minus in circle). The regarded area is limited to a radius of 75 nm as a good approximation.

IV. SUMMARY

Our measurements show that the relatively broad lines occurring in low-temperature single dot spectra of InP SAD in wetting-layer-type interfaces can be transformed into the expected sharp single dot spectra by increasing the temperature. These spectra consist of sharp photoluminescence emission lines connected with the δ-function-like density of states. They can be broadened with increased excitation intensity. The Coulomb interaction of the QD states with occupied trap states surrounding the dot explains the broadening conclusively by means of spectral diffusion, and the temperature-dependent change of the Fermi level is responsible for the switching of the appearance of the spectra. The dot can be seen as a probe for the surrounding charge configurations determined by the Fermi level. The origin of the trapping is most likely thickness variations of the WL. We present a model calculation for interacting and fluctuating charges which describes the low-temperature spectra qualitatively.

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[32] This system, however, is InP on (GaIn)P, grown by MBE instead of MOVPE, which might lead to a different structure of the WL as well, due to growth kinetics.