Screened Coulombic impurity bound states in semiconductor quantum wells

J. A. Brum and G. Bastard
Groupe de Physique des Solides de l'Ecole Normale Supérieure
(Laboratoire associé au Centre National de la Recherche Scientifique), 24 rue Lhomond, 75231 Paris Cedex 05, France

C. Guillemot
Centre National d'Etudes des Télécommunications, 22301 Lannion, France
(Received 2 December 1983)

The ground bound state of Coulombic impurity screened by free carriers in a quantum well versus the free-electron concentration n_e is calculated for several well thicknesses. Zero temperature and electric quantum limit are assumed. The random-phase-approximation dielectric function is used to describe the screening effect. For a given well thickness the binding energy decreases with increasing electron concentration until a saturation is reached at large n_e. The remaining binding is not negligible. At low temperature this may give rise to a freeze-out effect.

INTRODUCTION

There has been some interest in the determination of the binding energy of the hydrogenic impurities in nominally undoped semiconductor (SC) quantum wells (QW).[1-6] Photoluminescence experiments involving hydrogenic impurities have been reported.[1,2] The calculations of hydrogenic impurity levels squeezed in a quantum well are in qualitative agreement with experiments.[3-6] The intrinsic luminescence of high-quality QW's displays a clear excitonic behavior.[7,8] Similar to the impurity problem the carrier confinement along the growth axis increases the exciton binding energy over the bulk value.[8-10]

Optical experiments have also been performed in QW's containing free carriers. These carriers can be optically generated by intense illumination of a nominally undoped QW or can be of extrinsic origin. Some recent optical experiments have involved modulation-doped[11,12] or antimodulation-doped[13,14] GaAs QW's, where impurities are selectively placed in the cladding barrier or in the well, respectively. As a result of modulation doping there are free carriers in the QW. For antimodulation doping[13,14] the situation is unclear at low temperatures. In the presence of free carriers the Coulombic interaction is screened. In metal-oxide-semiconductor structures the bound states supported by screened Coulombic potentials have been extensively studied.[15-18] To our knowledge no such calculations are available for QW's. There are, however, noticeable advantages in studying screening effects in QW's. In these structures the doping control is quite advanced (selective doping appears to be possible) and the structural parameters (barrier height, well thickness) can be adjusted. The energy levels of both doped QW and of their impurities can be precisely measured and possibly accurately calculated. In the present communication we report the results of variational calculations of the ground-state binding energy of an isolated hydrogenic impurity placed at the center of SC QW's containing free carriers. Zero temperature and electric quantum limit are assumed in the evaluation of the random-phase-approximation (RPA) static dielectric function. We will show that the carrier confinement along the growth axis, which induces a concentration-independent Thomas-Fermi wave vector, leads to the persistence of a sizable impurity binding energy at high electron concentration. This result is in marked contrast with the bulk situation where the Coulombic binding energy vanishes beyond some critical carrier concentration. Although we calculate the binding energies of impurities in the presence of a given concentration of free carriers whose origin is not specified, there exist situations (antimodulation doping) where the value of the binding energy may feed back on the carrier concentration itself. We will only briefly discuss the occurrence of the carrier freeze-out in antimodulation-doped QW's.

DISCUSSION

Let us consider a quantum well of width L and barrier height V_b [Fig. 1(a)]. Because of the confining barrier, the z motion (z parallel to the growth axis) becomes quan-

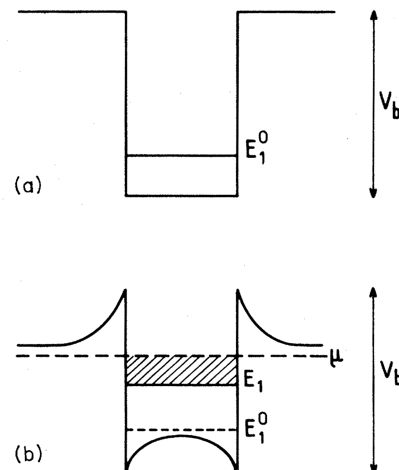

FIG. 1. (a) Conduction-band profile of an undoped semiconductor quantum well. (b) Conduction-band profile of a modulation-doped n-type semiconductor quantum well.

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tized. Let E_1^0 be the ground-state conduction subband. In the following we will neglect band nonparabolicity and assume a constant effective mass m^* throughout the whole structure. The ground-state wave function is then

$$\begin{aligned} \chi_1^0(z) &= A\cos(k_0 z)\ , \quad |z| < \frac{L}{2} \\ \chi_1^0(z) &= B\exp\left[-\kappa_b\left[z-\frac{L}{2}\right]\right],\quad z>\frac{L}{2} \\ \chi_1^0(z) &= \chi_1^0(-z)\ , \end{aligned} \tag{1}$$

with

$$\frac{\hbar^2\kappa_b^2}{2m^*} = V_b - E_1^0,\quad \frac{\hbar^2 k_0^2}{2m^*} = E_1^0\ , \tag{2}$$

and

$$k_0 \tan\left[k_0\frac{L}{2}\right] = \kappa_b\ . \tag{3}$$

In doped QW's the presence of free carriers as well as of charged impurities induces band bending.[19,20] Suppose that n_e electrons occupy the E_1 subband (electric quantum limit). In this limit the band bending can be treated perturbatively for sufficiently thin QW's.[20] To a good approximation, first-order nondegenerate perturbation on E_1^0 is sufficient. This approximation improves for decreasing n_e and is better in antimodulation-doped than in modulation-doped QW's. To this first order, the band bending leaves the eigenfunctions unchanged and shifts E_1^0. We will denote the perturbed energy by E_1:

$$E_1 = E_1^0 + \langle \chi_1^0 | -e\phi | \chi_1^0 \rangle\ , \tag{4}$$

where $\phi(z)$ is the self-consistent electrostatic potential due to charges. It includes the ionized impurities as well as the electronic contributions, the latter being treated in the Hartree approximation. The chemical potential μ at $T=0$ is

$$\mu = E_1 + \frac{\hbar^2 k_F^2}{2m^*}\ , \tag{5}$$

where the Fermi wave vector k_F is equal to

$$k_F = (2\pi n_e)^{1/2}\ . \tag{6}$$

We now consider the problem of the bound state associated with a single, isolated, impurity placed at the *center* of the quantum well (previous studies[3] have shown that on-center impurities statistically dominate the impurity-associated optical features when the impurities are randomly distributed in the well). The mobile carriers screen the impurity potential. In the random-phase approximation the screened Coulombic potential felt by the bound carrier may be Fourier expanded:[15]

$$V_s(\vec{r}) = \sum_{\vec{q}_\perp} V_s(\vec{q}_\perp, z) e^{i\vec{q}_\perp\cdot\vec{r}_\perp}\ , \tag{7}$$

where $\vec{q}_\perp, \vec{r}_\perp$ are two-dimensional wave vectors and $\perp$ refers to perpendicular to the growth (z) axis, i.e., in the layer plane. The average value over $(\chi_1^0)^2$ of the Fourier component $V_s(\vec{q}_\perp, z)$ is related to the corresponding average of the bare Coulombic potential by

$$\langle \chi_1^0 | V_s(\vec{q}_\perp, z) | \chi_1^0 \rangle = \frac{1}{\epsilon(q_\perp)} \left\langle \chi_1^0 \left| \frac{-2\pi e^2}{\bar{\kappa} S q_\perp} e^{-q_\perp |z|} \right| \chi_1^0 \right\rangle\ , \tag{8}$$

where S is the sample area, $\bar{\kappa}$ the lattice dielectric constant assumed to be the same throughout the whole structure, and $\epsilon(q_\perp)$ the wave-vector—dependent dielectric function. In the electric quantum limit at $T=0$ and neglecting damping, $\epsilon(q_\perp)$ is given by

$$\epsilon(q_\perp) = 1 + \frac{2}{a_0 q_\perp} f_s(q_\perp) g(q_\perp)\ , \tag{9}$$

where a_0 is the three-dimensional Bohr radius (~ 103 Å in GaAs). The screening form factor $f_s(q_\perp)$ is defined as

$$f_s(q_\perp) = \int\int dz\,dz' (\chi_1^0)^2(z) (\chi_1^0)^2(z') \times \exp(-q_\perp |z-z'|)\ . \tag{10}$$

The function $g(q_\perp)$ takes into account the finite size of the Fermi surface:

$$\begin{aligned} g(q_\perp) &= 1 \quad \text{if } q_\perp < 2k_F\ , \\ g(q_\perp) &= 1 - \left[1 - \left[\frac{2k_F}{q_\perp}\right]^2\right]^{1/2} \quad \text{if } q_\perp > 2k_F\ . \end{aligned} \tag{11}$$

Note that the presence of $g(q_\perp)$ in (9) is imperative in obtaining a reasonable description of the screened potential at low-carrier concentration and ultimately in ensuring the absence of screening if $n_e = 0$.[15]

Both $f_s(q_\perp)$ and $g(q_\perp)$ contribute to a decrease of the screening action at large wave vectors. As noticed by Price,[21] $f_s(q_\perp)$ can be safely approximated by

$$f_s(q_\perp) = [1 + C(L) q_\perp L]^{-1}\ , \tag{12}$$

where $C(L)$ is a C constant. The impurity Hamiltonian is

$$\mathscr{H} = \frac{p^2}{2m^*} + V_b Y(z^2 - L^2/4) - e\phi(z) + V_s(\vec{r})\ , \tag{13}$$

where $Y(x)$ is the step function, which is unity if $x>0$ and 0 otherwise. We have calculated the impurity binding energy by using the one-parameter trial wave function

$$\psi(\vec{r}) = N\chi_1^0(z)\exp(-r_\perp/\lambda)\ , \tag{14}$$

where N is the normalization constant and $\chi_1^0(z)$ the approximate (i.e., correct to first order in ϕ) ground solution of the doped quantum well defined in (1)—(4). The wave function (14) is separable in $r_\perp$ and z. We know[9] that (14) and some nonseparable trial functions (i.e., those obtained from (14) by changing $r_\perp$ into $(r_\perp^2 + z^2)^{1/2}$ gives very similar binding energies if $L/a_0 \lesssim 3$ and $V_b = \infty$ for unscreened Coulombic potential. We expect the same agreement for finite V_b, provided the well thickness is not too small. The separability in $r_\perp$ and z makes the knowledge of $V_s(\vec{r})$ unnecessary: Only the averages $\langle \chi_1^0 | V(\vec{q}_\perp, z) | \chi_1^0 \rangle$ are required. Therefore (8) can be

used, which greatly simplifies the algebra.

To distinguish between the respective actions of $f_s(q_\perp)$ and $g(q_\perp)$ it is illustrative to discuss first the case of an ideally two-dimensional problem. In terms of QW such a limit corresponds to letting $V_b=\infty$ and then $L=0$. Then

$$|\chi_1^0(z)|^2=\delta(z),\ \ f_s(q_\perp)=1\ . \tag{15}$$

The variational calculations reduce to the minimization of

$$E(t)=R_0\left[\frac{1}{t^2}-\frac{4}{t}\int_0^{\pi/2}\frac{\sin x\,dx}{\tan x+t\gamma(x)}\right],\ \ t=\lambda/a_0 \tag{16}$$

$$\gamma(x)=1\ \text{ if } x<\arctan(tk_Fa_0)\ ,$$
$$\gamma(x)=1-[1-(k_Fa_0t/\tan x)^2]^{1/2},\ \text{ if } x>\arctan(ta_0k_F)\ , \tag{17}$$

where R_0 is the three-dimensional effective rydberg. For large carrier concentration ($k_Fa_0 \gg 1$), one recovers the Thomas-Fermi limit and the screening becomes n_e independent. Therefore the binding energy saturates to a nonzero value ($\sim 0.56R_0$). This contrasts with the three-dimensional result where the binding energy vanishes when the Thomas-Fermi wave vector becomes comparable to $1/a_0$. When n_e goes to 0 ($k_Fa_0 \ll 1$), $E(t_{\min})$ goes to $-4R_0$, which is the binding energy of the two-dimensional, unscreened, hydrogenic potential. As shown in Fig. 2 the transition between the two regimes is rather smooth, extending over approximately three decades.

In the realistic case of QW of finite size, the results are qualitatively but not quantitatively similar to the ones obtained in a purely bidimensional situation (Fig. 3): The impurity binding energy decreases with increasing n_e and reaches a saturation value at large carrier concentration. This saturation value is smaller than found for $V_b=\infty$ and $L=0$: The finite extension of $\chi_1^0(z)$ along the growth axis leads to a decrease of the binding energy. This decrease overbalances the increased binding associated with the weakened screening due to the screening form factor $[f_s(q_\perp)\lesssim 1]$. The saturation value at large n_e is L dependent and decreases with increasing L: Increasing the well thickness tends to restore a bulk situation where we know that the binding energy of a screened impurity vanishes at large carrier concentration. Note, however, that for actual well thicknesses ($L \lesssim 200$ Å) the remaining binding is still sizable ($\sim 0.3R_0$) and should allow for the observation of impurity-associated features in doped QW's at low temperature. In fact, the participation of impurity to some luminescence lines in antimodulation-doped[13,14] or even modulation-doped[11] GaAs QW's has recently been reported (however, no detailed study of these impurity lines[11,13] is available at the moment).

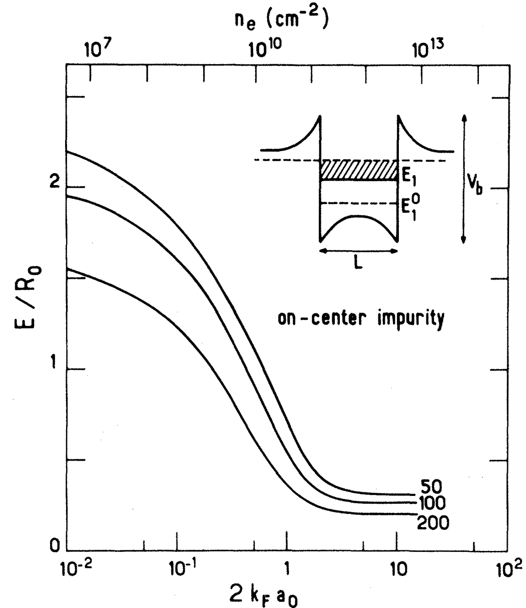

FIG. 3. The binding energy of a screened hydrogenic donor impurity placed at the center of a GaAs QW containing free carriers is plotted vs $2k_Fa_0$ for three different well thicknesses: $L=50$, 100, 200 Å. The material parameters used in the calculations are $V_b=0.2$ eV, $m^*=0.067m_0$, $a_0=103$ Å. $T=0$.

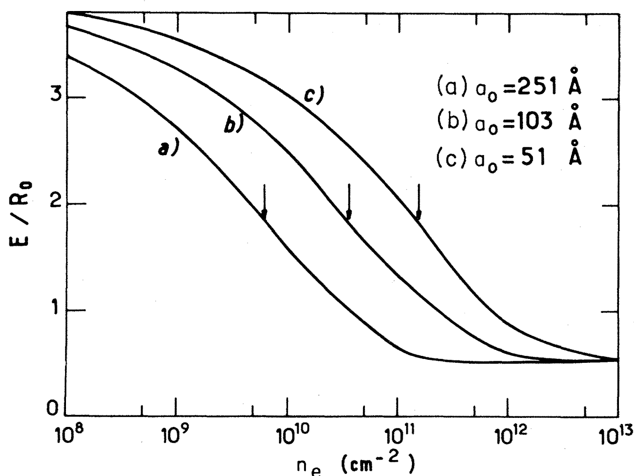

FIG. 2. Binding energy of a screened hydrogenic impurity in an ideally two-dimensional electron gas vs carrier concentration. Three different values of the three-dimensional Bohr radius a_0 are considered. The arrows indicate the concentrations for which the equality $2k_Fa_0=1$ is fulfilled.

The transition region between low and high n_e corresponds to $2k_Fa_0\sim 1$, i.e., to $n_e\sim 3.8\times 10^{10}$ cm^{-2} if GaAs parameters are used ($m^*=0.067m_0$, $\bar{\kappa}=13.1$). Hence, according to our calculations, one may expect to observe in low-doped QW samples ($n_e \lesssim 2\times 10^{11}$ cm^{-2}) some variation of the impurity binding energy with the carrier concentration.

Finally the persistence of a sizable binding energy at large n_e for actual QW thicknesses makes the freeze-out of carrier at low temperature a likely phenomenon in some doped QW samples. With respect to freeze-out, modulation-doped and antimodulation-doped samples should behave differently. In modulation-doped QW's ionized impurities are in cladding barriers and can be further separated from the QW itself by a spacer layer. They have released their carriers, which are mostly localized in the well. Although our calculations do not apply to this situation, we infer from previous studies[3] that the impurity binding energy will be negligible (since it is already very small for an unscreened potential[3]). Correspondingly, the

impurity wave function will be quite extended in the layer plane (several a_0). Band tailing will take place, adding a small impurity band tail on the low-energy side of the free-carrier density of states.[22] In antimodulation-doped samples the carriers and their parent impurities are both in the well. Our calculations, although done only for on-center impurities, show that $\sim 0.3R_0$ binding can be expected for actual L. This is ~ 1.6 meV, i.e., ~ 20 K in GaAs QW's. Hence for $T<20$ K appreciable freeze-out on isolated impurities should be expected. Many-impurity effects may again ruin the single-impurity behavior. However, for $L<200$ Å and $n_e<10^{12}$ cm^{-2} the extension of the impurity wave function in the layer plane is $\lambda_{\min}\lesssim 1.3a_0$, i.e., $\lambda_{\min}\lesssim 130$ Å in n-doped GaAs QW's. To continue to observe isolated-impurity effects when most of the carriers are unbound, the mean distance between impurities should be $\gtrsim 2\ \lambda_{\min}$. For a QW of width L, uniformly doped with N_d donors per cubic centimeter, the mean distance between donors in the layer plane is $(N_d L)^{-1/2}$. Hence isolated impurity behavior is not unexpected if $N_d<N_d^{\max}$ where $N_d^{\max}=(4L\lambda_{\min}^2)^{-1}$. With $L=100$ Å, $N_d^{\max}\sim 1.5\times 10^{17}$ cm^{-3}. In some recent experiments the net donor concentration was marginally smaller[13] or much smaller.[14] In Ref. 14 photoluminescence experiments were done at liquid-helium temperature and the freeze-out was probably complete. Hence the binding energies should have been close to the ones found in nominally undoped QW's of the same thickness. This is indeed what was observed.[14] In Ref. 13 the donor concentration was larger than in (14) ($\sim 10^{17}$ cm^{-3}) and the temperature was varied between ~ 5 and 20 K. At $T=20$ K some donors may have released their carriers. However, since at most 10^{11} cm^{-2} electrons were available, the saturation regime was not reached. Note finally that the analysis of thermal detrapping of the carriers in doped QW's can be intricate since the variation of the donor binding energy with n_e is substantial, and its rate of change is not smooth when $2k_F a_0\sim 1$.

CONCLUSION

We have calculated the binding energy of a single screened Coulombic impurity placed at the center of a doped quantum well. Our calculations show that the quasi-two-dimensional behavior of carriers in QW leads to binding energies which behave with the carrier concentration in a completely different way than is found in bulk materials. Namely, the binding energy does not vanish at large electron concentration but saturates to a finite (and sizable) value. Our calculations have taken into account finite barrier height but are valid only in the electric quantum limit. We believe that our results, derived for the impurity problem, are also qualitatively valid for the exciton problem. Finally, several assumptions made in the present calculations can be relaxed: One can study the binding energy versus the impurity position and include finite temperature or broadening in the dielectric function. These extensions are planned to be published elsewhere.

ACKNOWLEDGMENTS

One of us (J.A.B.) wishes to express his gratitude to Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq, Brazil) for financial support.

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