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SHALLOW IMPURITY SURFACE STATES IN SILICON

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Levine[1] has proposed an effective-mass model for shallow donors on semiconductor surfaces. His potential is $V=-e^2/\kappa r$ in the interior of the crystal, where κ is the dielectric constant, and $V=+\infty$ exterior to the crystal. The exterior potential is taken to be at $+\infty$ due to the high electron affinity of the crystal. However, two very important contributions to the potential have been omitted in his model. Because of the dielectric discontinuity of the surface, the potential[2] due to the impurity center is e^2/r reduced by the average of the exterior and interior dielectric constants rather than by just the interior κ, and there is also a potential[2] caused by the image charge of the excess electron. In a recent paper,[3] Petukhov, Pokrovskii, and Chaplik have used the same Hamiltonian that we use. They have made an error in that their image potential is too small by a factor of 2. They do not solve the exact Hamiltonian, but rather obtain solutions to an approximate hydrogenic Hamiltonian and then use first-order perturbation theory to account for the image potential, which has cylindrical symmetry.

Using our potential in the case of a high-dielectric-constant material with a clean surface, the effective dielectric constant for the impurity center is halved, and the image charge produces a repulsive potential in the interior which reduces the total potential up to 25% and reduces the symmetry from hemispherical to cylindrical. The resulting impurity states are somewhat deeper than those calculated from Levine's results. We have calculated the ground state and the four lowest optically excited states for a shallow donor in Si using an isotropic effective mass.

Our potential is

$$V=\frac{-2e^2}{(\kappa+1)r}+\frac{e^2(\kappa-1)}{2\kappa z(\kappa+1)} \quad z\geq 0, \tag{1a}$$

$$V=+\infty \quad z<0, \tag{1b}$$

with $\kappa=12.0$, $m^*=0.309m_0$.[4] The surface is taken to be at $z=0$, where z is distance perpendicular to the surface. Since $V=+\infty$ outside the crystal, the boundary condition on the wave function is $\psi(0)=0$. This requires that only those spherical harmonics may appear which satisfy

$$(l+m)=\text{odd}. \tag{2}$$

Since our potential (1) has cylindrical symmetry, the azimuthal quantum number m is a constant of the motion. We used the following variational functions for a given m:

$$\Psi=Nr^{m+1}e^{-r/a}\sum_{l=m+1}^{L}a_{lm}Y_{lm}, \tag{3}$$

where all the l's are either even or odd in order to satisfy (2). The ground state is the lowest $m=0$ state, since this state contains the lowest order Y_{lm} permitted by (2), namely,

Table I. Theoretical energies and radii of shallow surface and bulk donor states in Si.

$\|m\|$	E [a]	a [b]	E (Levine)[a]	E (Kohn)[a]
0	−11.20	63.91	−7.30	−29.0
1	−4.21	107.9	−3.24	−10.9
0	−2.00	331.7	−1.83	−8.8
1	−1.27	346.0	−1.17	−5.9
0	−0.76	866.8	−0.81	−5.7
				−2.9

[a]In units of 10^{-3} eV. [b]In units of a_0.

Y_{10}. The dipole selection rules are $\Delta m = 0, \pm 1$.

We have calculated the three lowest $m = 0$ and the two lowest $|m| = 1$ states. The $|m| \neq 0$ states are doubly degenerate.

In Table I we give our results, the energy levels calculated from Levine's work, and also those of shallow donors in the interior, as calculated by Kohn.[5] The convergence of the highest state is poorest, the highest $m = 0$ state calculated converging to about 1%. The lower states have converged to 0.1% or better. For the $m = 0$ states we took $L = 9$, and for the $|m| = 1$ states, $L = 10$ to attain this degree of convergence.

Using the expression of Petukhov, Pokrovskii, and Chaplik,[3] for the unperturbed energy, we calculate the ground-state energy to be -14.74×10^{-3} eV, and the two lowest excited states to be -6.55×10^{-3} eV. Their expressions for the perturbation energies are incorrect because of the above-mentioned error in potential. Furthermore, their first-order perturbation treatment is inadequate, particularly for excited states, as we have found that there is a substantial admixture of higher "l" states, which rapidly increases with the excited states. This admixture would be neglected in a first-order treatment.

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MULTIPLE-WAVE INTERACTIONS IN PIEZOELECTRIC SEMICONDUCTORS*

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This paper reports the observation of three- and four-phonon processes in cadmium sulfide. Previously, harmonic generation of ultrasonic waves in piezoelectric semiconductors and three-phonon interactions in solids have been reported.[1-4] However, to the best of the author's knowledge three-phonon processes in active media have not been observed to date, nor has there been any experimental confirmation of the four-phonon process in solids because of the extremely small signal levels involved. For the case of cadmium sulfide, however, a considerable increase in the signal-to-noise ratio is attainable due to its large effective third- and fourth-order elastic constants,[1] and because it is possible to use this material as its own amplifier.

In the usual small-signal analysis of the ultrasonic amplifier[5] the nonlinear interaction of the free carriers with the electric field accompanying the acoustic wave, as a result of the piezoelectric coupling, is neglected. In studying multiple-wave interactions this nonlinear cross term is retained resulting in the generation of new signals at the harmonics and sum and difference frequencies.[6,7]

For the observation of the three-phonon process, signals at 14 and 16 MHz were used to excite the input transducer, thereby generating two collinear acoustic waves in the CdS. Frequencies of 28, 30, and 32 MHz, some 30 dB smaller than the fundamentals, were detected at the output transducer by the heterodyning technique. The input and output transducers were resonant at 15 and 30 MHz, respectively. The difference frequency at 2 MHz was