[4]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[5]D. J. Stuckel and R. N. Euwema, Phys. Rev. B 1, 1635 (1970).

[6]R. C. Chaney, C. C. Lin, and E. E. Lafon, Phys. Rev. B 3, 459 (1971).

[7]B. O. Seraphin, Phys. Rev. 140, A1716 (1965); R. R. L. Zucca and Y. R. Shen, Phys. Rev. B 1, 2668 (1970); M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[8]This same model has recently been employed to study matrix elements in optical transitions. It was selected for its simplicity, but yields energy levels for important optical transitions within a few tenths of an eV of where we would choose them [see J. P. Van Dyke, Phys. Rev. B 5, 1489 (1972)].

[9]The zonal integration procedure is the same as that employed in Ref. 8. The OPW calculation is interpolated by parameterless $\vec{k}\cdot\vec{p}$ from six points in the Brillouin zone. However, since core bands are not readily incorporated in the $\vec{k}\cdot\vec{p}$ expansion [see J. P. Van Dyke, Phys. Rev. B 4, 3375 (1971)], the core eigenvalues are assumed independent of k and only the matrix elements interpolated. This means for core–conduction-band matrix elements the quantity actually being used is $\langle\Phi^{(\vec{k})}_{\text{core}}|\, e^{-i(\vec{k}-\vec{k}_0)\cdot\vec{r}}\nabla\,|\,\Phi^{(\vec{k})}_{\text{conduction}}\rangle$ where we want the matrix element without the exponential (k_0 is the point of $\vec{k}\cdot\vec{p}$ expansion). We considered this error by using less than six OPW points as well as by comparing matrix elements at points in the zone as found from different $\vec{k}\cdot\vec{p}$ expansion points and concluded that it was not significant enough to warrant adding additional OPW points or expanding the exponential as was done by J. Klima [J. Phys. C 3, 70 (1970)].

[10]Contrary to the assertion of Ref. 2, the transition is not forbidden at zone center to Γ_{15}. In the diamond structure the Γ_{15} symmetry admits d character as well as p character about the atomic site.

[11]A. B. Kunz, Phys. Rev. B 2, 5015 (1970).

[12]A. B. Kunz and N. O. Lipari, Phys. Rev. B 4, 1374 (1971), and references therein.

[13]R. J. Elliott, Phys. Rev. 108, 1384 (1957).

[14]N. O. Lipari and A. B. Kunz, Phys. Rev. B 3, 491 (1971).

[15]A. B. Kunz and N. O. Lipari, J. Phys. Chem. Solids 32, 1141 (1971).

[16]M. Cardona, W. Gudat, E. E. Koch, M. Skibowski, B. Sonntag, and P. Y. Yu, Phys. Rev. Letters 25, 659 (1970); C. W. Higginbotham, F. H. Pollak, and M. Cardona, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow*, 1968, edited by S. M. Rykin and Yu. V. Shmartsev (Nauka, Leningrad, 1968), Vol. 1, p. 57.

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Experimental Verification of the Surface Quantization of an *n*-Type Inversion Layer of Silicon at 300 and 77 °K

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The quantization of the motion, perpendicular to the surface, of electrons in an inversion layer at the surface of a silicon substrate is experimentally verified by accurate capacitance measurements at 77 and 300 °K. From the measurements the average distance of the electrons from the interface can be derived. To obtain agreement with the calculated value, the quantization has to be taken into account.

The electrons in an inversion layer at the surface of a p-type semiconductor are bound to the surface in a potential well caused by an externally applied electric field normal to the surface. The electron motion normal to the surface is therefore quantized.[1] Each energy level causes a two-dimensional subband, with the electron motion parallel to the surface being free. This quantization has been demonstrated at temperatures below 4.2 °K, by a number of experiments.[2–6] In this paper it is shown that quantization effects can also be measured up to room temperature by accurate capacitance measurements between the gate and the short-circuited source, drain, and bulk contacts of a metal-oxide–silicon-semiconductor transistor (MOST).

In the effective-mass approximation the electron motion in the z direction perpendicular to the surface is determined by Schrödinger's and Poisson's equation[7,8]

$$\left(-\frac{\hbar^2}{2m_z^j}\frac{d^2}{dz^2}-qV(z)\right)\psi_i^j(z)=E_i^j\psi_i^j(z), \tag{1}$$

$$\frac{d^2V}{dz^2}=\frac{q}{\epsilon}\left(N_A+\sum_{i,j}N_i^j\left|\psi_i^j(z)\right|^2\right). \tag{2}$$

E_i^j is the ith energy level of the electrons in valley j of the conduction band with effective mass m_z^j in the z direction. For a silicon (100) surface, we have two valleys with $m_z=0.98m_e$ and four with $m_z=0.19m_e$.[7]

The space-charge density in Poisson's equation

is determined by the ionized acceptor concentration N_A in the depletion layer $0 < z < w$, and the electron concentration $n(z)$ given by the sum in Eq. (2). N_i^j is the total number of electrons per unit square at energy level E_i^j and is given by[7]

$$N_i^j = \frac{m_{dj} kT}{\pi \hbar^2} \ln\left(1 + \exp \frac{E_{Fn} - E_i^j}{kT}\right). \quad (3)$$

m_{dj} is the density-of-states mass for the motion parallel to the surface of valley j; E_{Fn} is the quasi-Fermi-level for electrons in the inversion channel.

The boundary conditions for the equations are the following. The normalized wave functions ψ_i^j are zero at the surface and in the bulk of the material. The potential V at the edge of the depletion layer $z = w$ is equal to the potential in the bulk, while the electric field equals zero at $z = w$. The width of the depletion layer w is dependent on the difference between E_{Fn} and E_{Fb}, the quasi-Fermi-level for holes in the bulk. This difference may exist owing to an applied bias V_b between source and bulk contacts of the MOST.

We have solved Eqs. (1)–(3) numerically for different values of the dopant N_A, bulk bias V_b, and temperature T, as a function of the total number of electrons N_{inv} per square unit in the inversion channel, with an iterative method resembling the method of Stern.[9]

The average distance z_{av} of the electrons from the silicon surface can then be calculated from the known electron distribution $n(z)$. z_{av} will have an influence on the capacitance C between the gate and the ac short-circuited source, drain, and bulk contacts of the MOST. The total charge Q in the semiconductor is given by

$$Q = q(N_A w + N_{inv}), \quad (4)$$

and the total voltage drop V_{tot} is given by

$$V_{tot} = \frac{d_{ox}}{\epsilon_{ox}} Q + \frac{qN_A}{2\epsilon_{Si}} w^2 + \frac{q}{\epsilon_{Si}} z_{av} N_{inv} . \quad (5)$$

The oxide charge and the charge in surface states have been omitted; they only give a constant contribution in (4) and (5) in strong inversion, so they do not influence the capacitance.

The three terms in (5) are the potential drops over the oxide thickness d_{ox}, the depletion region, and the inversion region. Introducing the variation in the capacitance $\Delta C = C - \epsilon_{ox}/d_{ox}$, with $C = dQ/dV_{tot}$, and making use of the inequalities

$$N_A(dw/dN_{inv}) \ll 1, \quad z_{av} \ll d_{ox} , \quad (6)$$

we find after a straightforward calculation up to first order

$$z_{av} = \frac{\epsilon_{Si} d_{ox}^2}{\epsilon_{ox}^2} \Delta C - \frac{dz_{av}}{d \ln N_{inv}} - N_A w \frac{dw}{dN_{inv}} . \quad (7)$$

The variation in the capacitance ΔC is measured as a function of the applied dc gate voltage with a sensitivity of 0.001 pF.

Using Eq. (7), we can then measure the variation of z_{av} as a function of N_{inv}; the second and third terms on the right-hand side of Eq. (7) are correction terms, which are obtained from the numerical analysis.[10] The calculated values of z_{av}, together with the measured points, are given in Fig. 1 for different temperatures, bulk biases, and bulk dopants. One of the measured points must be matched, because only the variation of C and not its absolute value can be determined accurately enough. The dashed curves give the variation in z_{av} for a calculation which ignores the quantization in the z direction. The curves are shifted over a distance of + 15 Å for an easier comparison with he measured points which are matched to the solid urves.

The following remarks may be made.

(i) All measured points agree within experimental

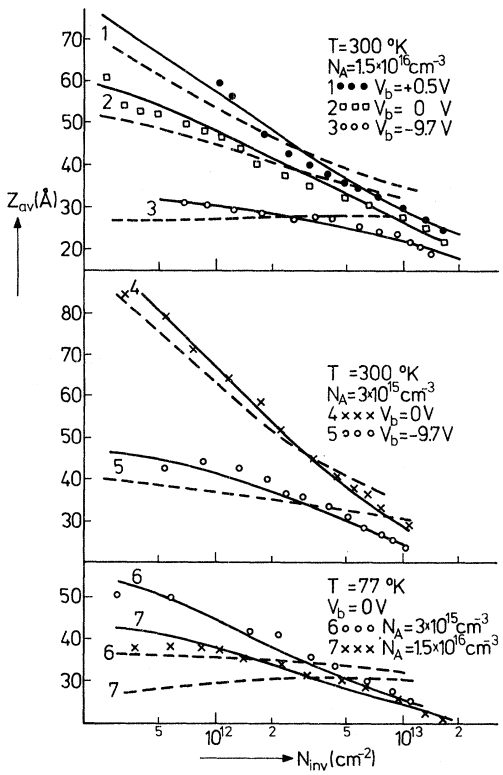

FIG. 1. Average distance of electrons from the interface z_{av} versus the total number of electrons N_{inv} in the inversion layer of (100) silicon surface. The dopant N_A of the substrate of the MOST, the temperature T, and the applied bulk voltage V_b are indicated in the figure. Solid curve, z_{av} calculated with quantization; dashed curve, z_{av} + 15 Å calculated without quantization. Circles, crosses, and squares are measured points.

error with the calculated values z_{av} taking the quantization into account. This over-all agreement is not obtained with the calculations without quantization.

(ii) A lower dopant N_A in the bulk causes a less steep potential well at the surface and increases z_{av}, as is seen from comparison of curves 2 with 4, 3 with 5, and 6 with 7.

(iii) Applying a forward bulk bias also decreases the steepness of the potential well and increases z_{av}; a negative bias does the reverse. Compare curve 1 with 2 and with 3, 4 with 5.

(iv) The difference between calculations of z_{av} with and without quantization being taken into account is less pronounced the less steep is the potential well and the higher the temperature. In the case of curve 4 the measurements do not enable us to distinguish between quantized or not quantized electrons. The energy separation of the quantized levels in this case is of the order of kT. If a negative bias is applied (curve 5) or the temperature lowered (curve 6), the distinction can clearly be made.

To sum up, the quantization of electrons in silicon inversion layers has been experimentally verified at 77 and 300 °K. All previous experimental work on this quantization has been done at temperatures of 4.2 °K and lower.

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[1]J. R. Schrieffer, in *Semiconductor Surface Physics*, edited by R. H. Kingston (Pennsylvania U. P., Philadelphia, 1957), p. 55.

[2]A. B. Fowler, F. F. Fang, W. E. Howard, and P. J. Stiles, Phys. Rev. Letters 16, 901 (1966).

[3]F. F. Fang and P. J. Stiles, Phys. Rev. 174, 823 (1968).

[4]M. Kaplit and J. N. Zemel, Phys. Rev. Letters 21, 212 (1968).

[5]D. Tsui, Phys. Rev. Letters 24, 303 (1970).

[6]R. G. Wheeler and R. W. Ralston, Phys. Rev. Letters 27, 925 (1971).

[7]F. Stern and W. E. Howard, Phys. Rev. 163, 816 (1967).

[8]E. D. Siggia and P. C. Kwok, Phys. Rev. B 2, 1024 (1970).

[9]F. Stern, J. Comput. Phys. 6, 56 (1970).

[10]J. A. Pals, Philips Res. Rept. Suppl. (to be published).

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Nonlinear Response of Bound Electrons to X Rays

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In the high-frequency limit, general expressions for second- and third-order induced electronic current densities in a medium are derived. These are valid for any medium with arbitrary spatial electronic-density variations. It is shown that the second-order current density at x-ray frequencies depends directly on the gradient of the unperturbed electronic density, so that it is sensitive to density variations both near the surface and near the ionic cores in a solid.

Recently, Eisenberger and McCall[1] have observed x-ray parametric conversion due to the lowest-order nonlinearity in a solid. This was proposed earlier by Freund and Levine.[2] They also considered theoretically the case of mixing of an intense optical wave with a wave at x-ray frequency.[3] Furthermore, an amplifier at such a high frequency leading to the availability of highly intense and monochromatic x-ray sources now seems to be a distinct possibility. It is, therefore, of some interest to examine critically the calculation of nonlinear susceptibilities of a solid at x-ray frequencies. Although, Eisenberger and McCall[1] and Freund and Levine[2] have tried to derive expressions for the second-order susceptibility in a solid at x-ray frequencies, we find that their results are not general enough to include the very significant effect due to the potential barrier at the surface of the solid.

Since x-ray photon energies are much higher than the surface barrier, we may argue that the effect of the surface should be negligible. However, in the high-frequency limit ($\hbar\omega \gg E_B$, where E_B is a typical electronic excitation energy for dominant transitions), we will show that the second-order