Surface Superconductivity and the Metal-Oxide-Semiconductor System

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Phonon-mediated and dynamically screened interactions between inversion-layer electrons in metal-oxide-semiconductor devices are studied. A numerical solution of the superconducting gap equation in the weak-coupling limit as a function of electron density for the Si(111)-SiO_2 system is given. Results are obtained for T_c which demonstrate that at high densities (with $T_c \lesssim 10$ mK), pairing is dominated by intervalley phonon exchange, whereas at low densities it is essentially due to exchange of electronic (plasmon, electron-hole) excitations.

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We present the structure and principal results of calculations of the superconducting properties of inversion-layer electrons in metal-oxide-semiconductor (MOS) devices. In recent years there has been considerable interest in the mechanisms of superconductivity at surfaces and interfaces, with a search for surface elementary excitations which would complement the role of bulk phonons in the pairing of quasiparticles. The complexity of most interface systems has, however, prevented substantial experimental and theoretical progress. The Si-SiO_2 interface in MOS systems seem particularly attractive for study: (i) A wealth of information[1] confirms that it is experimentally well controlled and theoretically simply treated in an "effective-mass" model[2,3]; (ii) the quasi-two-dimensional (2D) nature of the electron gas provides unusual features including a plasmon mode[4] with $\omega_p \sim q^{1/2}$ for small wave vector q; furthermore, the space quantization in the direction normal to the interface allows for typical electron-hole (e-h) intersubband excitations of the order of, and smaller than, the Debye frequency; and (iii) the electron density can be varied over two orders of magnitude.

We have constructed and solved the superconducting gap equation in the weak-coupling limit for the Si(111)-SiO_2 MOS device as a function of electron density. The novel aspects of our investigation include in particular the role of intervalley phonons inducing inversion-layer superconductivity, the finite-thickness effects, and the proximity of the interface. The principal result is that at high densities (~ 10^{13} electron/cm^2), intervalley phonon exchange allows for T_c's of order 10 mK. Other results follow from the rich variety of many-body effects which play unusual roles as the electron density is varied. For example, the dynamically screened Coulomb interaction can itself induce superconductivity, although this would occur at extremely low densities where other effects, such as surface roughness and impurity scattering, would be important. We make crude estimates of (vertex) corrections to the simple theory which tend to revise downward the estimates of T_c.

If the electrons are assumed to have an isotropic 2D effective mass m^*, and the 2D momentum variable $\vec{k}_\parallel$ is replaced by an energy variable such that $k = |\vec{k}_\parallel| = [(2m^*/\hbar^2)(\hbar\omega + E_F)]^{1/2}$, the gap equation is derived from a weak-coupling formation,[5] as

$$\Delta(\omega) = -\int_{E_F}^{\infty} \frac{d\omega'}{2\omega'} \tanh\frac{\hbar\omega'}{2k_b T_c} \Delta(\omega')K(\omega,\omega'), \quad (1)$$

with the kernel K given by

$$K(\omega,\omega') = \frac{A}{4\pi^2}\frac{2m^*}{\hbar^2}\int_{|k-k'|}^{k+k'} \frac{q\,dq}{kk'\sin\theta}\left[V^0(q) + \int_0^\infty \frac{2}{\pi}\,d\Omega\,\frac{\operatorname{Im}V^R(q,\Omega)}{\Omega + |\omega| + |\omega'|}\right] \quad (2)$$

for a device of area A and with $q \equiv |\vec{q}_\parallel| = (|\vec{k}_\parallel|^2 + |\vec{k}_\parallel'|^2 - 2|\vec{k}_\parallel||\vec{k}_\parallel'|\cos\theta)^{1/2}$. Equations (1) and (2) have already been used by Takada[6] in his study of the effect of the $q^{1/2}$ dispersion of surface plasmons on the superconductivity of a 2D system. Here it should be noted that, while finite-temperature fluctuations destroy the long-range order of a mean-field theory in two or less dimensions,[7] the calculation of the gap equation for the MOS system, where electrons are trapped within 20–100 Å of the interface, allows one, at least in principle, to obtain the temperatures at which the associated anomalies in transport phenomena might be expected. In our case $V^0(q)$ is the matrix element of the 2D Fourier transform of the Coulomb interaction $v(|\vec{q}_\parallel|; z, z')$ including the image potential,[8] and V^R is the irreducible

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e-e interaction as mediated by phonons, plasmons, etc.[9] The Coulomb matrix is calculated with simple MOS effective-mass wave functions[1,2]:

$$\psi_a(\vec{r}) = F_n(z)\varphi_a(\vec{r})\exp(i\vec{k}_{\parallel}\cdot\vec{r}_{\parallel}) \xrightarrow[n=0]{} (2\lambda^{3/2}/A^{1/2}) z e^{-\lambda z}\varphi_a(\vec{r})\exp(i\vec{k}_{\parallel}\cdot\vec{r}_{\parallel}), \tag{3}$$

where $\varphi_a(\vec{r})$ is the Bloch function for the ath conduction-band minimum in the bulk band calculations and $F_n(z)$ the variational solution of an effective-mass equation,[10] with the lowest subband solution for $n=0$. The electron density per unit area, ρ, ranges from 10^{11} ($r_s = 7.3$) to 10^{13} cm^{-2} ($r_s = 0.73$) while the inverse profile thickness λ satisfies $\lambda = (15\pi\rho/8a^*)^{1/3}$, where $a^* = \epsilon_{\rm Si} h^2/m_{zz}e^2$ is the effective Bohr radius with the effective mass of the valleys in the direction normal to the interface.[10] In the Si(111)-SiO_2 system, the electrons occupy six equivalent valleys in the paramagnetic ground state, resulting in six elliptical Fermi lines, which are replaced by equal-area circles for convenience.

The matrix elements of the direct Coulomb interaction (V^0) as well as of the dynamically screened e-e interaction ($V_{\rm Coul}{}^R$) for the lowest and first-excited subbands are calculated using the wave functions of Eq. (3) and a formulation of self-consistent surface screening as developed in other contexts.[8,11] Intervalley contributions have already been shown to be small for MOS systems[10] and thus only intravalley terms are retained. The plasmon and electron-hole contributions to the e-e interaction are contained within the intrasubband and intersubband contributions to the susceptibility, respectively.

We have also made detailed microscopic calculations of the phonon-mediated terms.[12] Arguments based on a continuum expansion[13] show that the intravalley phonons provide a weak interaction which can be cast in the form [cf. Eq. (2)] $K(\omega=0,\omega'=0) = -0.01|D|^2 r_s^{-2/3}$, where the appropriate deformation potential D is expressed in rydbergs, and is typically less than unity. But as in bulk calculations,[14] we find a large attractive contribution from intervalley phonons—hence our choice of the Si(111) orientation. The phonon contribution to V^R in Eq. (2) is given by

$$V_{\rm ph}{}^R(\vec{q}_{\parallel},\omega) = -\sum_j \frac{2h\omega_j(\vec{q}_{\parallel})|g_j(\vec{q}_{\parallel})|^2}{[h\omega_j(\vec{q}_{\parallel})]^2 - (h\omega)^2}, \tag{4}$$

where j denotes the branches and q_z values. We calculate $V_{\rm ph}{}^R$ in full using (i) a simple two-parameter force-constant model for the phonons, with a ratio of bond-bending to bond-stretching parameters of 0.7 (cf. Lax[15]), which we think is an adequate (short-range) model at the large q's involved in the intervalley contribution; (ii) a fourth-nearest-neighbor tight-binding Hamiltonian expanded over a basis of antibonding orbitals for the electrons in the conduction bands[16] (so as to reproduce the minimum); (iii) a microscopic formulation of the surface screening function[9,12] as used in the calculation of the electron-phonon matrix elements g_j in Eq. (4); and (iv) a parametrized form of the Si pseudopotential $V_{\rm ion}$ consisting of the $1/r$ attraction plus a repulsive term of the form $\beta e^{-\alpha r}/r$ with parameters ($\beta = 1.5$, $\alpha^{-1} = 1.7$ a.u.) chosen to fit the bulk pseudopotential. The electron-phonon matrix element $g_j(\vec{q}_{\parallel})$ coupling electrons at the centers of valleys a and b is given by

$$g_j(\vec{q}_{ab}) = \int \psi_b{}^*(\vec{r})\Big[\int \epsilon^{-1}(\vec{r},\vec{r}\,')\sum_{\rm sites}\delta\vec{R}_j\cdot\nabla V_{\rm ion}(\vec{r}\,'-\vec{R})\,d^3r'\Big]\psi_a(\vec{r})\,d^3r, \tag{5}$$

where $\delta\vec{R}_j$ is the displacement of site $\vec{R}$ due to the phonon mode $(\vec{q}_{ab}, j)$. Calculations have been performed on a 24-layer slab of silicon bounded by (111) surfaces to which both free and periodic boundary conditions normal to the slab have been applied. The free boundary is chosen as a first approximation to the actual MOS interface for the calculation of the phonon exchange.[17] The inclusion of the (amorphous) SiO_2 would involve an inordinate computational effort merely to provide the phonon modes on the silicon side of the interface. A significant enhancement in $V(\vec{q}_{\parallel},0)$ occurs with the use of free boundary conditions: In this case, with q_z no longer a good quantum number, the selection rules for phonon scattering are relaxed, so that more modes can couple (although they individually couple more weakly), with a net result that more than compensates for the loss of phase coherence for the contributions from each unit cell that a bulk selection rule would guarantee. With a careful consideration of the normalizations used in effective-mass theory, we find that, with free boundary conditions, [cf. Eq. (2)] $K(\omega=0,\omega'=0) = -0.22 r_s^{-2/3}$ for which the coefficient is 30% greater than the equivalent calculated with the periodic boundary conditions. Thus, the static phonon-mediated exchange at-

traction is enhanced near a surface. We use the free boundary condition kernel below arguing that the loss of q_z as a good quantum number should be followed by the loss of $\vec{q}_\parallel$ (which is retained in our calculation) because of the proximity of the amorphous SiO_2. At worst we are modestly overestimating the enhancement by using our free boundary conditions. The gap equation (1) is solved numerically by matrix inversion, breaking up the integration interval into smaller ranges.[6]

The results for the transition temperature T_c as a function of the density parameter r_s are displayed in Fig. 1. The kernel K is calculated for three cases: In curve a, only the intrasubband contribution ($n=0$) to the susceptibility is taken into account in the irreducible interaction V^R, with the phonon kernel put equal to zero. We note a threshold for pairing mediated by intrasubband excitations only at about $r_s=3$, and a maximum in T_c occurs for higher values of r_s. This is due to the fact that T_c contains a factor E_F (proportional to r_s^{-2}) and also the usual exponential factor involving the interaction which increases with r_s. This result corresponds to a certain extent to Takada's calculation,[6] but with

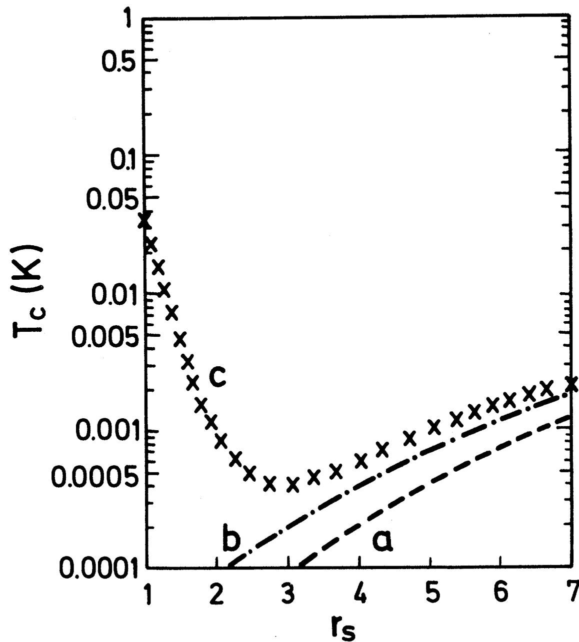

FIG. 1. Calculated results for T_c vs r_s for the Si(111)-SiO_2 MOS device. In curve a only intrasubband excitations are taken into account in the kernel $K(\omega, \omega')$; in curve b intrasubband plus intersubband excitations are considered; and in curve c the phonon-mediated interaction is added to the purely electronic interactions.

the inversion-layer thickness incorporated. In curve b we include the first excited subband, and we see that the T_c's are further enhanced, indicating that ***e-h*** excitations similar to those discussed in the "exciton mechanism" of superconductivity[9] play an active role in the quasiparticle pairing. Finally, in curve c the interaction V^R also includes the phonon-mediated contribution. Intervalley phonons provide the dominant pairing mechansim at high densities (i.e., $r_s \simeq 1$, reaching $T_c = 0.098$ K at $r_s = 0.7$ by which density most devices have reached dielectric breakdown). This result provides an upper limit for T_c to the extent that free boundary conditions overestimate the phonon attraction, and at these densities the use of the kernel derived from periodic boundary conditions yields a lower bound for T_c ($r_s=1$, $T_c = 0.002\,°K$; $r_s = 0.7$, $T_c = 0.011\,°K$). This large reduction is due to the strong interference of $K^{ph}(0, 0) = -0.16$ and $K^{Coul}(0,0) = +0.095$ (at $r_s=1$) which is typical of the cancellations encountered in weak-coupling superconductivity calculations. We see that a surface enhancement of K^{ph} is important in producing T_c's that are measurable in experimentally accessible electron-density ranges. We do not consider the more widely studied Si(100)-SiO_2 system as an attractive example because only intravalley phonons can contribute to the phonon kernel. Other potential materials for replacing silicon include InAs, PbTe, and possibly $SrTiO_3$ (which shows bulk superconductivity under doping), although the technical problems in fabricating high-quality interfaces are considerable. From our calculation, we have a clear picture that the surface tends to increase the superconducting possibilities.

Our results must be considered as order-of-magnitude estimates (as is the case for most T_c calculations) because of the approximations that have gone into constructing the kernel for the MOS system, and because of the effects of higher-order (vertex) corrections to the mean-field theory used here. Electron-hole ladder diagrams,[16] which enter the screening ϵ^{-1}, have a significant effect on the e-e interactions at the larger values of r_s: This correction is indispensible for the correct short-range behavior of the pair-correlation function.[18] Strong-coupling corrections have been estimated in several ways with the general trend being a reduction of the weak-coupling T_c by a factor of about 3 in the range $1 < r_s < 6$. The paramagnon effect, producing an unfavorable effect on the s-wave coupling of the Cooper pair,[19] was found (for a dispersion-

less interaction) to decrease the irreducible e-e interaction V^R by about 15% at $r_s = 1$. Fluctuation effects can be discussed to a certain extent along the lines of Aslamov and Larkin[20] and Maki.[21] However, the novel feature of this system is the fact that the electron density also controls the thickness of the inversion layer and the "excess conductivity" resulting from pairing due to thermal effects in the normal phase could in principle be used to monitor the squeezing out of the third dimension as a function of density. Interface roughness and disorder, which become important at larger r_s, and the competition with other broken symmetries (such as Wigner crystallization, which is under much discussion in related 2D systems[22]) will be discussed in a subsequent paper.[17]

In summary, we have demonstrated the possibility of superconducting pairing in MOS devices, highlighting the density dependence of the various coupling mechanisms. The Si(111)-SiO_2 system is the most favorable of the current generation of MOS devices, but the use of other materials, with higher bulk electron-phonon matrix elements, could further enhance the range of temperature and other variables over which superconducting phenomena would be observed. It is hoped that the present investigation might prompt experimental work to complement that on bulk doped semiconductors.

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Depth-Selective Conversion-Electron Mössbauer Spectroscopy

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A high-resolution, electrostatic electron spectrometer combined with a Mössbauer spectrometer has been used to obtain depth-selective ^{57}Fe Mössbauer spectra from the surface region of an iron scatterer by detecting emitted conversion electrons at selected electron energies. Clear experimental evidence of a sharp depth resolution in the Mössbauer spectra is demonstrated for the first time, in accordance with theoretical predictions.

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In recent years there has been an increasing interest in conversion-electron Mössbauer spectroscopy (CEMS) as a useful, nondestructive technique for studying surface metallurgy, corrosion, or ion-implanted surface layers because of the small penetration depth of low-energy elec-

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