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Schottky barrier and contact resistance at a niobium/silicon interface

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Electrical transport properties of niobium-silicon contacts are reported over a wide doping range. It is found that a short low-energy argon plasma sputtering of the silicon surface prior to metal deposition lowers the Schottky barrier height by 0.12 eV, without degrading diode ideality. This result is interpreted as a partial explanation for the dependence of the superconducting proximity effect in semiconductors on sputter cleaning.

Recently considerable interest in superconducting field-effect devices has developed.^{1,2} A highly successful device, in which a supercurrent flowing through heavily doped silicon is controlled by a gate electrode, has been reported by Nishino *et al.*¹ Here superconductivity is induced in the semiconductor by the proximity effect, i.e., the leakage of Cooper pairs into the semiconductor. The Cooper pair density at a certain distance from the interface depends on two factors³: first, the transmission of Cooper pairs across the semiconductor-semiconductor interface, and second, the decay length of the superconducting order parameter in the semiconductor. Systematic experimental results have only been obtained on the latter.^{1,2,4} For the degenerate case results can be understood by treating the semiconductor as a normal metal.³ So far the role of the transmission probability at the interface has received very little attention. For a substantial proximity effect one aims at a transmission probability close to 1. In the case of interest, i.e., at low temperatures and high impurity concentrations the transport mechanism will be tunneling. Consequently one expects that the Cooper pair density in the semiconductor will be very small, and the proximity effect will be effectively quenched. However, substantial supercurrents are observed^{1,2,4} as well as a superconducting energy gap in silicon in Nb/Si bilayers.⁵ It is a common experience that the proximity effect is sensitive to the interface conditions. A sputter clean of the semiconductor surface prior to metal deposition has proven to be an essential prerequisite for the observation of supercurrents.^{1,2,6} In this letter we report measurements of Schottky barrier heights and contact resistances of niobium on *n*-type silicon and discuss the influence of sputter cleaning.

The samples are fabricated on low-resistivity *n*-type Si (100) wafers with 4- μm -thick $1 \times 10^{15} \text{ cm}^{-3}$ phosphorus-doped epitaxial layers. Into a 400-nm-thick SiO_2 layer contact windows of sizes 8.2×10^{-5} and $3.24 \times 10^{-4} \text{ cm}^2$ are cut by standard photolithography. Different doses of phosphorus are implanted in the contact areas. After removal of the implanted top layer of the oxide the wafers are annealed at 975 °C for 90 min to achieve a flat doping profile over the first 200 nm. The back contact is formed by evaporation of Al, followed by annealing at 450 °C in pure N_2 for 30 min.

The wafers are broken into two halves. One half is to be subjected to *in situ* sputter cleaning prior to niobium deposition, while the other is not. Immediately before loading into the vacuum chamber the wafers are given a 2% HF dip for 15 s to remove the native oxide, followed by a short rinse

in de-ionized water. Background pressure in the vacuum chamber is below 1×10^{-6} Torr. Sputter cleaning is done by exposure to an Ar plasma for about 5 s with ion impact energy of 350 eV at a power density of 1 W/cm². Niobium is deposited by dc magnetron sputtering in an argon atmosphere at a rate of 6.5 nm/s. The niobium target is presputtered for several minutes. Contact pads are patterned by CF_4/O_2 plasma etching. Niobium thicknesses ranging from 20 to 200 nm are used. Results for all thicknesses are essentially the same. In the following we will mainly discuss results on thin samples, with 20–40 nm niobium and 30–40 nm SiO_2 insulation.

The Schottky contacts are analyzed by the current-voltage method,⁷ where the current I is given by the thermionic emission-diffusion transport equation:

$$I = AA^{**}T^2 \exp(-e\Phi_{Bn}/k_B T) \times \exp[e(V - IR_s)/nk_B T], \quad (1)$$

with A the diode area, A^{**} the effective Richardson constant, taken to be $120 \text{ A cm}^{-2} \text{ K}^{-2}$, T the temperature, Φ_{Bn} the Schottky barrier height (image force lowering included), V the applied bias, R_s the series resistance, and n the ideality factor. k_B and e have the usual meaning.

Measurements were performed at room temperature. Typical I - V curves for nonsputtered samples are shown in Fig. 1. They have good linearity over two to three orders of magnitude, with ideality factor 1.07. Uniformity over the

FIG. 1. Current-voltage characteristics for large Nb/Si Schottky contacts at several doping concentrations (no sputter clean before Nb deposition).

wafer is good, although slight differences in reverse current are observed. For the lowest doping the barrier height is found to be 0.60 eV. The large and small contacts have identical values of Φ_{bn} and n . The ratio of the zero bias current densities for large and small contacts, J_{OL}/J_{OS} , ranges from 0.85 to 0.93, indicating a small leakage current for small contacts.

With increasing doping concentration Φ_{bn} gradually decreases. At 10^{18} cm^{-3} a more rapid change is observed and n increases (see Table I). This indicates the onset of tunneling of thermally excited carriers through the top of the barrier. This behavior is in agreement with the thermionic emission theory.⁷

Figure 2 shows the effect of sputter cleaning on the I - V curves of the Schottky contacts. The sputter-cleaned samples have conductivities almost two orders of magnitude higher. The absence of a distinct linear portion in the forward current is due to voltage loss over the series resistance. Fitting the characteristics of the sputtered samples to Eq. (1) yields $\Phi_{bn} = 0.48 \text{ eV}$ and $n = 1.06$. The current density ratio J_{OL}/J_{OS} equals 1.0, indicating negligible leakage currents. In addition I - V curves of different contacts on the same wafer are identical. The variation of Φ_{bn} and n for higher doping concentrations is analogous to the non-sputtered case (Table I).

For doping levels higher than 10^{18} cm^{-3} the characteristics gradually become ohmic, and determination of Φ_{bn} with Eq. (1) is no longer possible. Instead we measured contact resistances at zero bias. Table II contains results for sputtered and non-sputtered samples. In agreement with the lower Schottky barrier for the sputtered contacts a lower contact resistance is observed in this doping range. For the highest doping the contact resistance is dominated by the substrate series resistance.

The effect of sputtering is to lower the Schottky barrier height by as much as 0.12 eV, which is paralleled by a reduction in contact resistance. The importance of the barrier lowering for the tunneling transmission can be estimated by considering the expression for the WKB tunneling probability⁷

$$|T^2| = \exp(-e\Phi_{bn}/E_{00}), \quad (2)$$

with $E_{00} = (eh/4\pi)(N_d/\epsilon_0\epsilon_r m^*)^{1/2}$, where N_d is the impurity concentration, ϵ_r the semiconductor dielectric constant (11.9 for Si), m^* the tunneling effective mass (0.916 times the electron rest mass for n -type Si at 4.2 K), h Planck's constant, and ϵ_0 the permittivity in vacuum.

TABLE I. Schottky barrier height Φ_{bn} and ideality factor n at various doping levels N_d , for samples with and without sputter cleaning prior to niobium deposition.

$N_d \text{ (cm}^{-3}\text{)}$	Non-sputtered		Sputtered	
	$\Phi_{bn} \text{ (eV)}$	n	$\Phi_{bn} \text{ (eV)}$	n
1×10^{15}	0.60	1.08	0.48	1.06
1×10^{16}	0.58	1.08	0.48	1.09
5×10^{16}	0.57	1.07	0.46	1.09
1×10^{17}	0.56	1.07	0.46	1.09
1×10^{18}	0.50	1.4	0.41	1.3

FIG. 2. Comparison of I - V curve for a sputtered (dashed curve) and a non-sputtered sample (solid curve).

For $N_d = 1 \times 10^{19} \text{ cm}^{-3}$ the transmission probability is enhanced by sputtering by a factor of 850, for $N_d = 1 \times 10^{20} \text{ cm}^{-3}$ by a factor of 8.4. Obviously the transmission of electrons for sputtered samples is substantially improved, facilitating the diffusion of Cooper pairs into the silicon. However, it must be noted that the absolute values of the tunneling probability remain very small: 9.4×10^{-10} for $N_d = 1 \times 10^{19} \text{ cm}^{-3}$ and 8.3×10^{-3} for $N_d = 1 \times 10^{20} \text{ cm}^{-3}$ (including image force lowering). Hence, even though the transmission is increased these numbers are still orders of magnitude below the value of order 1, required by conventional proximity effect theory.

Although the sputter treatment is motivated by the desire to clean the surface, we do not believe that the barrier lowering is a result of removal of contamination. Inspection with Auger spectroscopy of the substrate surface after HF dipping revealed the presence of very little oxygen and carbon, about 10% and 5% of a monolayer, respectively. So the lowering of Φ_{bn} is not due to the removal of a surface layer, but rather to sputter damage. The incident Ar ions cause defects at the silicon surface. These will give rise to a higher density of states in the band gap at the interface, leading to pinning of the Fermi level at a higher energy.

It is noteworthy that the sputter damage does not deteriorate the diode behavior of the contacts. The low ideality factors indicate that the current is still of thermionic emission type, and the reverse current shows no enhanced leak-

TABLE II. Comparison of contact resistance R_c for samples with and without sputter cleaning prior to niobium deposition (small contacts).

$N_d \text{ (cm}^{-3}\text{)}$	$R_c \text{ (}\Omega \text{ cm}^2\text{)}$	
	non-sputtered	sputtered
1×10^{17}	7.6	0.17
1×10^{18}	0.93	3.5×10^{-2}
1×10^{19}	0.12	2.5×10^{-2}
5×10^{19}	3.7×10^{-2}	1.9×10^{-3}
1×10^{20}	2.5×10^{-3}	2.4×10^{-3}

FIG. 3. Effect of aging for (a) non-sputtered and (b) sputtered contacts. Solid curves: measured within two days after fabrication. Dashed curves: after six weeks.

age current. The induced defect states could in principle give rise to a nonthermionic current contribution by acting as generation-recombination centers. However, because of the low energy of the Ar ions the defects will be confined to the first few atomic layers of the silicon. Therefore, the probability of electron tunneling from the silicon bulk to a defect state will be as low as for an electron tunneling directly to the metal. Consequently the defect mediated current is negligible also. So the only observable effect of the induced defects is the lowering of the interface potential barrier.

In addition we find that sputtered samples show a higher resistance against deterioration in time. Figure 3(a) compares current-voltage curves of an unsputtered sample mea-

sured a few days after fabrication and of the same sample after six weeks of storage in air. Rectification is strongly degraded, and the forward current has a pronounced non-thermionic leakage current at low bias. In contrast Fig. 3(b), the same comparison for a sputtered sample, demonstrates that the characteristic is hardly affected by the lapse of time. This difference in behavior between normal and sputtered samples is typical for thin samples, but is absent for thicker Nb films, suggesting that the deterioration is due to diffusion of oxygen atoms through the films.

In summary, we have investigated the influence of an *in situ* Ar plasma sputter clean on the Schottky barrier of Nb on *n*-Si substrates in the doping range 10^{15} – 10^{20} cm $^{-3}$. It is found that the barrier height, 0.60 eV without sputtering, is lowered by 0.12 eV. Good diode ideality is preserved, while uniformity and stability are improved. We interpret the change in barrier height not as a result of cleaning, but of surface damage. The barrier lowering offers a qualitative explanation for the favorable influence of sputtering on the superconducting proximity effect in semiconductors, but the enhanced tunneling probability as such is not sufficient to explain the experimentally observed proximity effect.

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