Electron correlation effects in transport and tunneling spectroscopy of the Si(111)-7 \times 7 surface

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Electronic properties of the Si(111)-7 \times 7 surface are studied using four- and two-probe conductivity measurements and tunneling spectroscopy. We demonstrate that the temperature dependence of the surface conductivity corresponds to the Efros-Shklovskii law in the entire temperature range 250 - 10 K studied. The energy gap at the Fermi level observed in tunneling spectroscopy measurements at $T \geq 5$ K vanishes by thermal fluctuations at $T \approx 30$ K, without any sign of the metal-insulator transition. We show that the low-temperature energy gap observed by the tunneling spectroscopy technique is actually the consequence of the Coulomb blockade effect.

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INTRODUCTION

Electron transport in low-dimensional materials is one of the major topics of condensed matter physics. Reducing dimensionality of physical objects may change qualitatively their properties. The atomic size scale is the natural limit for size reduction. Massless Dirac particles in graphen \textsuperscript{1}, surface superconductivity \textsuperscript{2}, various one-dimensional systems with Luttinger liquids \textsuperscript{3} are well known examples. At such scales electron correlation effects often start to dominate.

The self-assembled superstructures on semiconductor surfaces have wide potentialities for experimental study of the electron transport in one- and two-dimensional systems. The scanning tunneling spectroscopy (STS) is often used to identify the electronic structure of the ground state of these surfaces with atomic resolution. But the electron correlations can induce appreciable distortions in the STS spectra \textsuperscript{4}. The effect is enhanced on the low conductive system with sheet conductivity much less than minimum metallic conductivity $1/R_h = e^2/h = 39\mu S$.

A striking example is the Si(111)-7 $\times$ 7 surface, one of the most comprehensively studied structures. On the one hand, the surface has a metallic band structure revealed by the low temperature angle-resolved photoemission spectroscopy (ARPES) \textsuperscript{5}. On the other hand, a hard energy gap at the Fermi level ($E_F$) is observed at low temperatures with STS \textsuperscript{5,7}. The experimental data from nuclear-magnetic-resonance \textsuperscript{8}, high resolution electron-energy-loss spectroscopy \textsuperscript{9}, high resolution photoemission \textsuperscript{10}, and transport measurements with micro four-point probe (MFPP) technique \textsuperscript{11} also hint to a gap between 0 eV to 0.2 eV at low temperatures. Possible reasons for the gap opening are suggested to be formation of the charge-density waves or Mott-Hubbard insulator ground state. Similar discrepancy between metallic surface band structure revealed by ARPES \textsuperscript{11} and nonmetallic electron transport behavior \textsuperscript{12}, a hard gap singularity at $E_F$ by STS at low temperatures \textsuperscript{13} was also observed for the Si(111)-$\sqrt{3}$ $\times$ $\sqrt{3}$-Sn surface.

In this Letter we report the results of detailed study of the temperature evolution of the tunneling density of states (TDOS) and conductivity of the Si(111)-7 $\times$ 7 surface in a wide-temperature range. No evidence of any phase transition for this surface down to helium temperatures is observed. Instead, the temperature variation of the surface conductivity follows the Efros-Shklovskii law over the entire temperature region studied. This hoping conduction caused by the development of a soft Coulomb energy gap is in obvious contradiction with known STS results \textsuperscript{6,7}. We argue that the hard-like energy gap observed in STS \textsuperscript{5,7} does not correspond to the true local density of states, but is actually the Coulomb anomaly modified by charging effect in the surface. Two various models that describe the obtained tunneling spectroscopy data are provided. We consider that similar disagreement between nonmetallic conductivity and the gap in STS spectra at low temperatures are common for most low-conductive surface reconstruction with ‘metallic’ surface band (Sn, Ag, K on Si(111) and Ge(111) and others) and could be explained by localization and Coulomb blockade effect.

EXPERIMENTAL

We studied n-type Si(111) samples with $\rho = 0.1 \, \Omega \cdot \text{cm}$ and $\rho = 1 \, \Omega \cdot \text{cm}$ for transport measurements. The clean Si(111)-7 $\times$ 7 surface was prepared by direct current degassing at $T \approx 900$ $^\circ$C for 12 hours followed by flashing up to 1250$^\circ$C for 10 seconds and slow computer-controlled cooling down. The quality of the Si(111)-7 $\times$ 7 surface was controlled by STM. Conduction measurements were performed \textit{in situ} in the home-built four-probe system \textsuperscript{15}, mounted on a cold finger of UHV cryogenerator SHI-APD Cryogenics. The system operates from room
temperature to the 35 K. The probes were made from optic fiber wires \((d = 20 \mu m)\) covered with Ta conduction film. The distance between the probes was 100 ± 20 \(\mu m\). Four conducting probes assembled on the special holder in the linear geometry were approached to the surface by piezodrivers simultaneously until electric contact to the surface was obtained for all the probes. The current \(I\) flows between the outer pairs of probes and the voltage drop \(\Delta V\) was measured between the inner pair of probes. The conductivity

\[
\sigma_{4p} = \frac{\ln 2}{\Delta V} \frac{I}{l}
\]

was measured from the slope of the linear current-voltage curves \((I-V\) curves) collected during slow temperature sweeps, which takes about 6 hours in one direction. Accuracy of the temperature measurements was verified by a calibrated thermometer mounted onto the sample holder and placed instead of a silicon sample. The two-probe measurements where performed separately using Omicron LT SPM with modified standard tip holder, equipped with two 50 \(\mu m\) platinum wires. This method let us to extend the range of the studied conductivity down to \(10^{14}\Omega\), which is hardly available for the four-probe study. The distance between contacts \(l\) was 1 mm. The \(I-V\) curves were measured at fixed sample temperatures. The conductivity is

\[
\sigma_{2p} = \frac{I}{\pi V} \ln \left( \frac{l}{d} \right)
\]

where \(d\) is a characteristic size of the contact area. This equation accounts for the geometrical spreading resistance and implies absence of an energy barrier between the platinum wires and the surface. We take \(\ln(l/d) \approx 10\) which corresponds to \(d = 1 - 1000\) nm within 30\% accuracy. The contribution of the bulk into the measured conductivity value was found to be negligibly small in our samples at low temperatures: a control measurement obtained for 1 mm distance between probes shows that \(\sigma_{4p}\) is reduced by more than 2 orders of magnitude during temporary vacuum degradation at the \(T = 200\) K [14]. This gives the bulk contribution to be below 1\%. Further reduction of the bulk contribution is obtained by reduction of the distance between probes [15] by an order of magnitude, as well as by decreasing the temperature. Thus, no significant contribution of the bulk in our results is expected.

The tunneling spectroscopy measurements were performed in UHV LT STM Omicron. We studied \(n\)- and \(p\)-type Si with \(\rho = 1\) \(\Omega\-cm\). Such crystals are insulating in the low-temperature region and cannot be studied by the standard methods. Therefore, for STS study we used the external illumination to produce necessary bulk conduction (see details in [6]). All STS measurements were performed with platinum STM tips. The \(I-V\) curves were collected at fixed temperature over the central adatom of the Si(111)-7 \(\times\) 7 unit cell and averaged over series of measurements consisting of tens individual cycles each of 1000 points back and forth. Differential conduction was calculated numerically from the averaged \(I-V\) curves.

**RESULTS**

Figure [1] shows the temperature dependencies of the Si(111)-7 \(\times\) 7 surface conductivity measured on \(n\)-type samples with different room-temperature resistivity. The conductivity variation exceeds eight orders of magnitude in the temperature range \(250-10\) K. Our results indicates that the Efros-Shklovskii law

\[
\sigma = \sigma_0 \exp \left( - \left[ \frac{T_{ES}}{T} \right]^{2} \right)
\]

fits conductivity of the Si(111)-7 \(\times\) 7 surface much better than any other law, such as \(\sigma \propto \exp(-[T_0/T]^{1/3})\) corre-
sponding to the 2D variable-range hopping conduction or a simple activation law as it was proposed in the previous publication [11], where the temperature dependence was studied at \( T > 100 \) K and conductivity variation slightly exceeds one order of magnitude.

Temperature sets of the tunneling \( dI/dV \) spectra near the surface Fermi level measured on both \( n \)- and \( p \)-type Si(111)-7 \times 7 samples with \( \rho = 1 \ \Omega \cdot \text{cm} \) are shown in Fig. 2. The Fermi level is shifted by the surface photovoltage due to external illumination [3]. The low-temperature data obtained at \( T = 5.6 \) K corresponds to the energy gap \( 2\Delta = 40 \pm 10 \) meV reported earlier [4]. We see that the gap smears quickly with the temperature increase and nonzero DOS at the Fermi level is getting visible for both for \( n \)- and \( p \)-type silicon samples at \( T \gtrsim 30 \) K.

DISCUSSION

According to [17], in the system described by hopping conduction, the electrons are localized and this is the Coulomb interaction that turns the conductivity into the Efros-Shklovskii conductivity regime. Experimental value of the parameter \( T_{ES} = 0.55 \pm 0.05 \) eV is approximately the same for all studied crystals for both 4- and 2-probe techniques. The activation energy at \( T = 10 \) K, \( \frac{1}{2} \sqrt{T_{ES} T} \approx 10 \) meV, is noticeable lower than \( \Delta \). The localization length of electrons is

\[
\xi = \frac{2.8e^2}{\kappa T_{ES}} = 6.9 \text{Å}
\]

where \( \kappa = 11.8 \) is the Si dielectric constant. The obtained value is in a good agreement with the model [18], where electrons responsible for the conductivity were proposed to be localized on dimers (\( \approx 6 \) Å length) of the Si(111)-7 \times 7 surface.

The tunneling data seems to be in the obvious contradiction with the measured temperature variation of the surface conductivity and band structure obtained by ARPES [5]. Indeed, the Efros-Sklovskii law [1] corresponds to the soft gap at the Fermi level (Fig. 3a) [17]

\[
g(\varepsilon) \sim \frac{2 \kappa^2}{\pi e^4} |\varepsilon - E_F|,
\]

whereas the observed gap [6, 7] is obviously hard-like.

The origin of this discrepancy is related to very low conductivity value of the studied surface, \( \sigma \ll e^2/h \). This leads to appearance of the zero-bias anomaly due to a finite time required for tunneling electron to leave the tunneling region, so that the tunneling DOS \( (dI/dV \) spectra) does not correspond any more to the intrinsic DOS of a studied system, and therefore cannot be considered as its local DOS. For a diffusive conduction it leads to the logarithmic suppression of TDOS, \( dI/dV \propto \ln|V| \) [4]. To describe the TDOS of the Si(111)-7 \times 7 surface demonstrating the various-range hopping conduction we employ
the theory of the dynamical Coulomb blockade \[19, 20\]. The theory accounts for the impedance of the equivalent electrical circuit in the tunneling current calculations. The respective circuit consisting of tunneling junction in series with an arbitrary external impedance \(Z_{\text{ext}}(w)\) is shown in (Fig. 2b). In our experimental scheme \(Z_{\text{ext}}(w) = 1/(i\omega C + R^{-1})\), where \(C\) and \(R\) are equivalent capacity and resistance of the surface. The tunneling current is calculated for the total impedance seen from the tunneling junction side, which is a parallel combination of \(Z_{\text{ext}}\) and \(C_T\), and is given by

\[
Z(w) = [i\omega C_T + Z_{\text{ext}}^{-1}(w)]^{-1} = [i\omega C_{\Sigma} + 1/R],
\]

where \(C_{\Sigma} = C + C_T\). The \(dI/dV\) characteristics evaluated analytically according to \[19\] are plotted in Fig. 2 with green dotted line. As \(R = 10^7 - 10^{13}\Omega\) is known from our conductivity measurements, so \(C_T\) is the only fitting parameter which is required to describe the entire data set shown in Fig. 2. The tunneling capacity was estimated to be not higher than \(C_T \approx 0.3 \cdot 10^{-19}\) F and therefore can be neglected. The best fit of our data was obtained for \(C = 1.8 \cdot 10^{-18}\) F.

As seen from Fig. 2 the dynamical Coulomb blockade theory describes the experimental data inside the gap region fairly well, but it predicts an additional density of states above the gap edges. This disagreement is eliminated when the presence of the soft gap is taken into account (Fig. 3a) in addition to the Coulomb blockade effect.

In our case, the capacitance \(C\) determines the barrier \(e/2C\) for tunneling of the next electron. This modifies the Coulomb gap (2) in TDOS spectra in a way which is presented in Fig. 2 of Ref. \[20\] at \(R/R_0 = \infty\) (see Fig. 3b). Then the localization region \(a\) of tunneled electron is \(a \sim C/8\pi\varepsilon\varepsilon_0 \simeq 6.9\) Å. The value completely coincides with the localization length obtained from the transport measurements.

The verification of the proposed model is comparison of the predicted and observed values of the logarithmic slope \(\ln(dI/dV)' \equiv d\ln(dI/dV)/dV\). This derivative reflects the sensitivity of \(I-V\) curves to thermal fluctuations. In a simple case of tunneling between the tip and the surface with the DOS shown in Fig. 4 the tunneling current is given by

\[
I = D \int_{-\infty}^{+\infty} g_s(\epsilon) g_t(\epsilon + eV) \left( \frac{1}{1 + e^{\frac{\epsilon}{kT}}} \right) \left( 1 - \frac{1}{1 + e^{\frac{\epsilon}{kT}}} \right) d\epsilon
\]

\[
- D \int_{-\infty}^{+\infty} g_s(\epsilon) g_t(\epsilon + eV) \left( 1 - \frac{1}{1 + e^{\frac{\epsilon}{kT}}} \right) \left( 1 + e^{\frac{\epsilon}{kT}} \right) d\epsilon
\]

(3)

where \(g_t\) is the density of states in the metallic tip, \(g_s\) is the surface density of states of the simulated system represented on Fig. 4, \(D\) is the transmission coefficient and \(\alpha\) is the phenomenological parameter (see below). If \(kT \ll 2\Delta\) and bias voltage \(eV \lesssim \Delta\), the tunneling current will flow in this case due to tunneling from surface.
states below the energy gap into the small tail $kT$ wide of unfilled states in the metallic tip. This smears out the gap edges and decreases the slope of the $dI/dV$ curves close to the energy gap edges region. The dependence of the slope $dI/dV$ on the temperature is

$$\frac{e}{k} \frac{1}{\ln(\frac{dI}{dV})} \approx \alpha T.$$  \hspace{1cm} (4)

The inverted slopes of the data of Fig. 2 averaged over intervals $V_\pm = -20 \pm 10$ mV and $V_+ = 20 \pm 10$ mV are presented in Fig. 3. As seen, the experimental slope $\alpha$ is 2.5 times larger than the expected value $\alpha \approx 1$. Taking it into account, we tried to fit the entire set of our data by using Eq. 3 with $\alpha \neq 1$. The best fit is obtained for $2\Delta = 40$ meV and $\alpha = 2.5$ and provides quite reasonable approximation of the data in the entire voltage region (black dotted line in Fig. 2), whereas the Coulomb blockade model fits the data in the gap region only. That points out that the gap is actually not hard. Indeed, the low-voltage conductance in the Coulomb blockade case obeys the power law, $I \propto V^\beta$ [20], which can be hardly distinguished from the exponent if $\beta \gg 1$ (in our case $\beta \approx 4$ at 10 K). So our model (Fig. 3) may be used as a reasonable approximation of the experimental results not only in the gap region but also at $V > \Delta$. Further study, both experimental and theoretical, required to develop a self-consistent model which describes tunneling into low-conducting surface with hopping conduction applicable to entire bias voltage range.

CONCLUSION

In conclusion, through analysis of surface conductivity measurements and tunneling spectroscopy data, we found that the Si(111)-7 \times 7 surface is 2D system with electron localization and strong electron-electron interaction effects. The Coulomb interaction defines the temperature dependence of the surface conductance that corresponds to the Efros-Shklovskii conduction in the whole studied temperature range. The experimentally obtained localization length of the electron agrees with the one suggested earlier. We also demonstrate that DOS measured by tunneling spectroscopy in the Si(111)-7 \times 7 surface differs from the intrinsic surface density of states due to the environmental Coulomb blockade effect. Two different phenomenological models describing the fast thermal spreading the gap edges are presented. We consider that the observed difference between intrinsic DOS and DOS obtained from tunneling spectroscopy is a general phenomena in a wide class of low-conducting surfaces.

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