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RESONANT TUNNELING THROUGH CHEMISORBED HALOGEN ATOMS ON AG(111)

by

JOACHIM HOSSICK SCHOTT AND HENRY S. WHITE

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University of Minnesota  
Department of Chemical Engineering and Materials Science  
Minneapolis, MN 55455



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# Resonant Tunneling through Chemisorbed Halogen Atoms on Ag(111)

Joachim Hossick Schott and Henry S. White

Department of Chemical Engineering and Materials Science  
University of Minnesota  
Minneapolis, MN 55455

Tunneling spectroscopy measurements performed with a scanning tunneling microscope (STM) on Ag(111) surfaces coated with a monolayer of halogen atoms (F, Cl, Br and I) are reported. Maxima in the tunneling spectra are assigned to resonance tunneling through both the occupied p- and virtual bound states of the halogen adatoms. The observed minimum tunneling resistance at resonance is  $\pi\hbar/e^2$  (~12.6 k $\Omega$ ), in agreement with theoretical predictions.

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Ever since the pioneering work of Tsu, Esaki and Chang<sup>1,2</sup>, resonant tunneling has been recognized as an important mechanism of electrical transport through media containing localized electronic states. The flow of current through such systems is maximized whenever the energy of the incident electrons is closely matched to the energy of the localized electronic states. Kalmeyer and Laughlin<sup>3</sup> have theoretically shown that the minimum resistance,  $R$ , in the energetic vicinity of a resonance is  $(\pi\hbar/e^2)1/T$ , where  $T$  denotes the transmission probability. The latter quantity may approach unity at resonance (see also: Landauer<sup>4</sup>). Consequently, regions of negative differential resistance may exist in the energy range between resolved resonances.

Current research on resonant tunneling is focussed on two-dimensional<sup>5</sup> and one-dimensional<sup>6</sup> semiconductor quantum well structures. However, resonant tunneling and related phenomena are also of great importance in metal-adsorbate systems, in particular in regard to photoinduced desorption of adsorbed species<sup>7</sup> and electron field-emission from such systems<sup>8,9</sup>. Reports of resonance tunneling phenomena observed with the scanning tunneling microscope (STM) are comparatively rare<sup>10-12</sup>. A phenomenon closely related to resonant tunneling is observed in the STM when the tip and the metal form a one-atom point contact<sup>13-15</sup>. In this case, Lang<sup>13</sup> has shown that the resistance  $R$  is again of the form  $(\pi\hbar/e^2)A$ , with the factor  $A$  being dependent on the identity of the tip-atom, but of order unity.

In this report, we present strong evidence for resonant tunneling through chemisorbed halogen atoms observed using an STM, operated in air and at room temperature. The samples investigated in this study are Ag(111) surfaces coated with a complete monolayer of halogen atoms ( $X = F, Cl, Br$  and  $I$ ). The spatial structures of the halogen monolayers can be atomically resolved by STM and are described in a previous report<sup>15</sup>. The halogen coating was prepared by immersing a flame annealed, (111) faceted Ag sample in a concentrated acidic halogen solution (consult ref. 16 for details).

No carbon or oxygen contaminations could be detected using Auger electron spectroscopy, even after several hours of exposure to ambient air.

Tunneling spectroscopy (TS) and microscopy experiments were performed with a modified Nanoscope II scanning tunneling microscope<sup>17</sup>, in which the tip was held at virtual ground and the bias voltage was applied to the sample. Tips were mechanically cut from flame annealed PtIr wire. In the TS experiments, the tunneling current  $I$  was measured as a function of the applied bias voltage  $V_b$ . The tunneling current  $I$  was recorded after current-voltage conversion across a  $10\text{ k}\Omega \pm 1\%$  resistor in series with the tip and passing the signal through a 1:1 operational amplifier (input impedance  $> 10^{12}\ \Omega$ ). The bias voltage was also recorded after passing the signal through a 1:1 operational amplifier. The tip was placed in the center of a surface area which was imaged before and after a sequence of I-V measurements to ensure that no surface damage occurred during I-V measurements. Before the actual measurement, a tip-sample distance,  $s$ , was established by adjusting the feed-back loop of the instrument with a programmable gap-resistance,  $R_{set} = V_{set}/I_{set}$ . The feed-back loop was then disabled and the tunneling current was measured as a function of the applied voltage, which was a triangle shaped ramp. The voltage ramp initially proceeded towards positive voltages. Typical scan times were  $\sim 2$  sec per full cycle.

Fig. 1 shows a typical current voltage traces obtained for a Cl-coated Ag(111) facet. We note several striking features of these I-V curves. 1) The tunneling current increases sharply above a positive sample bias threshold (Fig. 1a); for negative voltages between  $-0.5\text{ V}$  and  $0\text{ V}$ , however, the current is virtually zero, as is evident from the current trace shown in the insert in Fig. 1b. (This latter trace was obtained with a  $1\text{ M}\Omega$  resistor in series with the tip; note the nA-current scale in the insert). 2) The curve in Fig. 1a exhibits current plateaus and/or peaks which are frequently accompanied by regions of negative differential resistance. 3) At voltages more negative than  $\sim -1.4\text{ V}$ , the current

rises again sharply (Fig. 1b) and a broad peak is observed at  $\sim -2.1$  V with a current level of  $\sim 165 \mu\text{A}$ . 4) For high positive and high negative bias voltages (in excess of  $+0.5$  V and  $-2.5$  V, respectively) the tunneling current reaches the limit set by the  $10 \text{ k}\Omega$  resistor (Fig. 1a and 1b). 5) At positive bias voltages, the I-V curves exhibit a pronounced hysteresis between the upward and downward voltage scans, e.g. Fig. 1a. The hysteresis is less pronounced in the negative bias voltage region (Fig. 1b).

We note that severe surface and/or tip damage often occurs upon starting the voltage ramp at values around  $-2$  V, most likely because of tip instabilities due to the extremely high current levels obtained in this bias voltage region (Fig. 1b). However, some tips reproducibly yield the features of the current trace shown in Fig. 1b without inducing damage, and the general phenomenon, i.e., the high current level at  $V_b \sim -2$  V, is reproducible with any tip. The I-V response in the positive region (Fig. 1a) can be reproduced numerous times with a particular tip over a particular surface area without inducing tip or surface damage, provided that the positive voltage scan limit is kept below  $\sim +0.5$  V. We therefore exclude mechanical tip-sample contact as the cause of the unusually high current levels measured in our experiments at positive and negative biases. We also rule out vibrationally assisted tunneling as a possible explanation since the expected inelastic contributions to the total current are much too low<sup>18</sup>.

To understand the I-V curves shown in Fig. 1, it is necessary to consider the potential energy contours at the Ag-halogen interface under the influence of the electric field between tip and sample. The theoretical work of Lang and Williams<sup>19</sup> indicates that the broadened 3p-level of the chemisorbed Cl atom lies  $\sim 2.5$  eV below the Fermi-energy of the metal and is therefore totally occupied (ionic adsorption). At zero bias, the potential energy contours between tip and sample may then be depicted as in Fig. 2a. For small negative values of  $V_b$ , tunneling will proceed mainly from the filled portion in the tail of the broadened 3p Cl-ion level into empty states of the tip. The expected current density is

low because of the low density of states in the tail of the 3p level, in agreement with the I-V curve shown in the insert of Fig. 1b. For more negative values of  $V_b$ , the Ag-Cl bond length increases, as shown by Bagus and Paccioni<sup>20</sup>. Upon changing the Ag-Cl bond length, the Cl-3p level tracks the potential energy contour of the metal surface<sup>19</sup>. Therefore, as the ion moves away from the surface, the 3p level moves up in energy, as depicted in Fig. 2b. Thus, the available emitter density of states increases, resulting in an increase in the tunneling current, in agreement with Fig. 1b. When the center of the Cl-3p level passes the tip Fermi level, a *resonance* peak may be observed in the I-V spectrum, the energetic position of which is shifted upward with respect to its equilibrium position. We believe that the broad current shoulder at  $\sim -2.1V$  (i.e., at approximately 1eV below the substrate Fermi-level) in the I-V curve in Fig. 1b is due to such a resonance.

For small positive bias voltages, tunneling will mainly proceed from the Fermi-level of the tip to empty states in the tail of the 3p level. Since there are virtually no such states, the current is essentially zero and the junction is blocking. At higher positive biases, electrons can now *resonantly* tunnel from filled tip states into empty Ag states, *via virtual bound state levels in the Cl potential well*, as depicted in Fig. 2c. Whenever the energy of the incident electrons matches the energy of such bound states, a peak in the I-V spectrum should occur, in qualitative agreement with the I-V curve in Fig. 1a. Following Kalmeyer and Laughlin<sup>3</sup>, the minimum resistance  $R$  at resonance should be  $\pi\hbar/e^2$  ( $\sim 12.6\text{ k}\Omega$ ). Inspection of Figs. 1a and 1b reveals that the minimum resistance observed at a resonance peak is indeed  $12.6\text{ k}\Omega$  (see also Figs. 3 and 4). Considering that with further increasing bias voltage (either positive or negative), more and more chemisorbed Cl atoms can act as a resonator for the tunneling (or field emitted) electrons, it is clear that there will be an increasing resonant background current. Therefore, the

current will be quickly limited by the  $10\text{k}\Omega$  resistor upon increasing the bias voltage beyond the resonance onset.

Fig. 3 shows that the onset of the resonance current depends strongly on the tip-sample separation, which is proportional to the gap resistance  $R_{\text{set}} = U_{\text{set}}/I_{\text{set}}$ . For larger tip-sample separations the resonance onset occurs at higher bias voltages. This finding suggests that the resonance tunneling is very sensitive to variations in the shape of the local potential energy contours, as expected. Since a small thermal drift is always present in STM experiments, this also explains our observation that the resonance onset scatters by  $\sim \pm 25\text{mV}$  between subsequent measurements, in which all parameters were kept constant.

Similar I-V curves are also observed for Ag(111) facets coated with monolayers of other halogens (I, Br, and F). As an example, Fig. 4 shows a typical curve obtained from a F-coated sample. Again, pronounced resonance peaks are seen for moderately high positive bias voltages as in the Cl-case, and the minimum resistance at resonance is  $\sim (\pi\hbar/e^2)$ .

Finally, we address the hysteresis observed in the I-V curves. Goldman et. al.<sup>21</sup> have observed a similar phenomenon with semiconductor quantum well structures, which has been attributed to a charge-storage induced bistability in the quantum well<sup>22,23</sup>; some of the charge which is injected into the potential well during the first half cycle of the voltage scan remains stored in the well, resulting in a shift of the resonance level energies in the second half cycle of the scan. Thus, a double valued current voltage curve is obtained. The hysteresis observed in our experiments at positive and negative biases may in part be associated with barrier fluctuations due to mechanical and thermal instabilities. However, a change in the structure of the chemisorbed layer beneath the tip, due to the local electric field (e.g., the change in the Ag-Cl bond length<sup>20</sup>), may also account for the observed hysteresis.

In summary, we have described the behaviour of a resonance tunneling diode of atomic dimensions. The predominant features of the I-V behaviour are qualitatively well understood upon applying the principles of double barrier resonance tunneling<sup>1,2,9</sup> to the theoretical model of halogen-chemisorption on metal surfaces<sup>19</sup>.

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## Figure Captions

**Fig. 1.** Typical tunneling spectroscopy I-V traces obtained on a chlorine coated Ag(111) facet. a) Set point bias ( $V_b$ ) and tunneling current ( $i_t$ ):  $V_b = -0.07V$ ,  $I_t = 11nA$ . b)  $V_b = -0.65 V$ ,  $I_t = 5nA$ . The curve in the insert was obtained in a different experiment using a  $1M\Omega$  resistor in series with the tip (same set point resistance). All other curves were obtained with a  $10k\Omega$  resistor. Note the different scales.

**Fig.2.** Schematic potential energy profiles in the tunnel junction. The broadened Cl-3p level is indicated by the bell-shaped distribution in the potential well between tip and sample. a) Unbiased tunnel junction. b) Negative (sample) bias. c) Positive (sample) bias.  $E_n$  sketches the virtual bound states.

**Fig.3.** I-V traces obtained on a chlorine-coated Ag(111) sample for different initial set point resistances (as indicated). This sequence was obtained with the same tip over one particular surface location (neglecting small thermal drift). Time difference between subsequent measurements:  $\sim 60$  sec. (see text).

**Fig.4.** Typical tunneling spectroscopy current voltage trace obtained on a fluorine-coated Ag(111) facet.  $V_b = -0.9 V$ ,  $i_t = 5 nA$ .

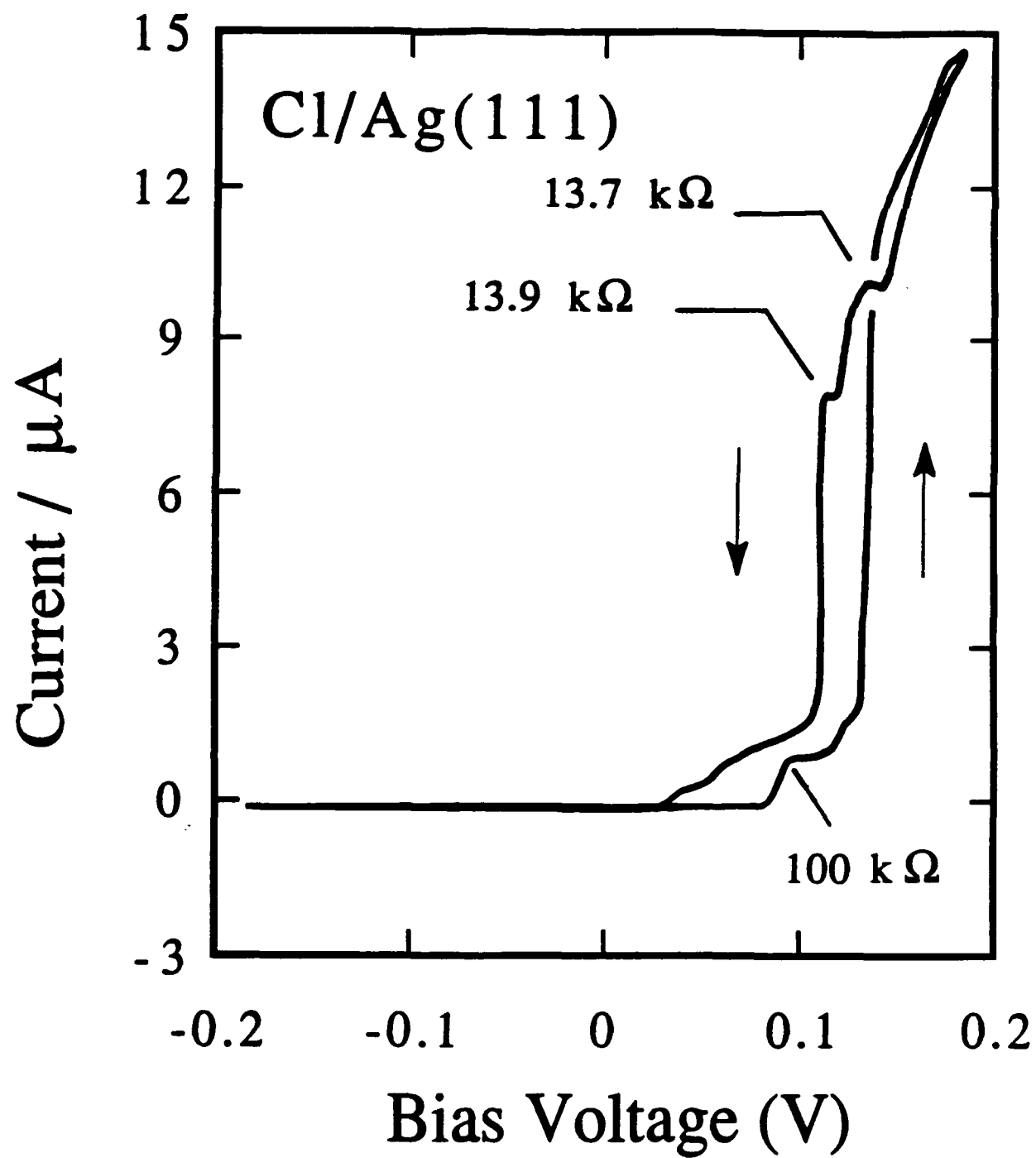


Fig. 1a

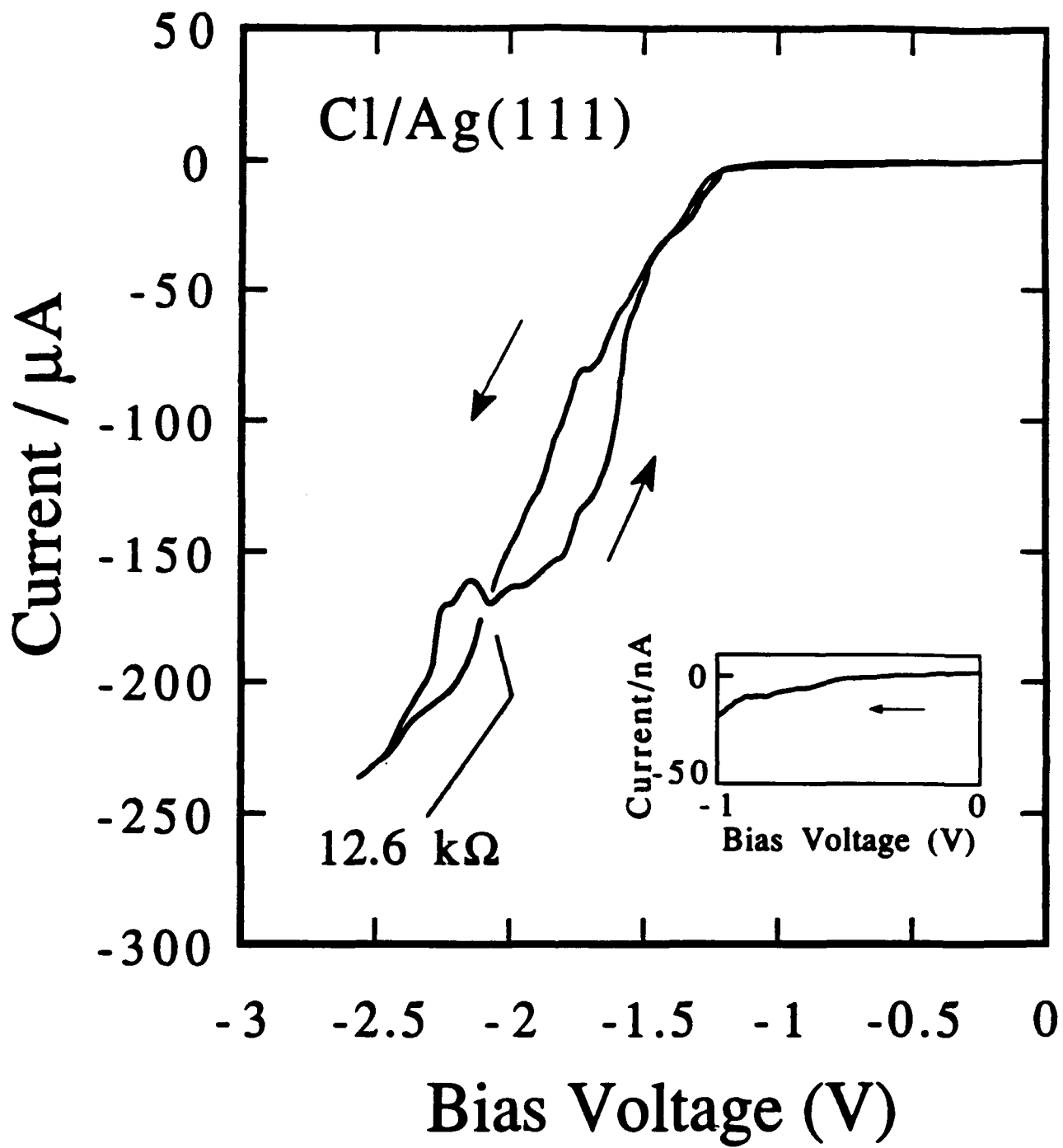
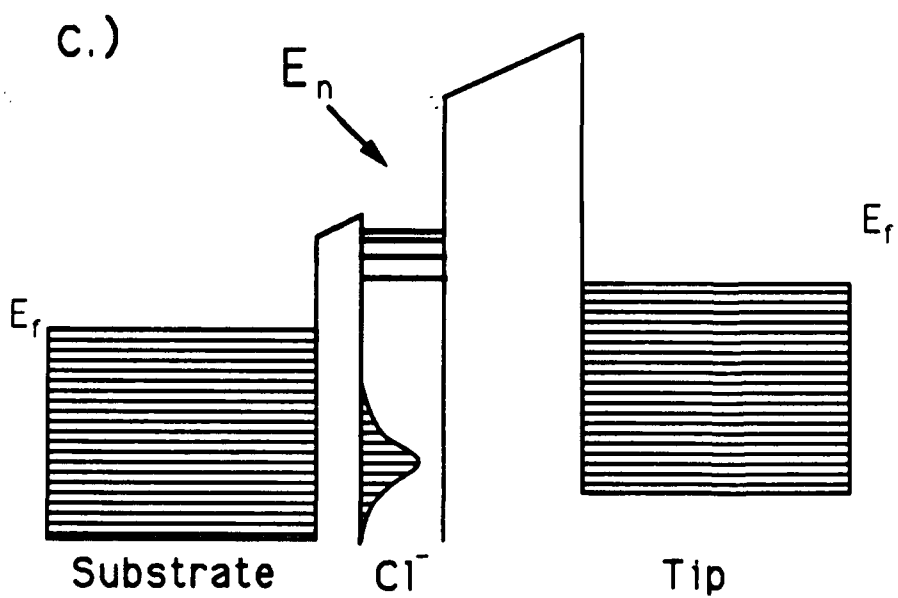
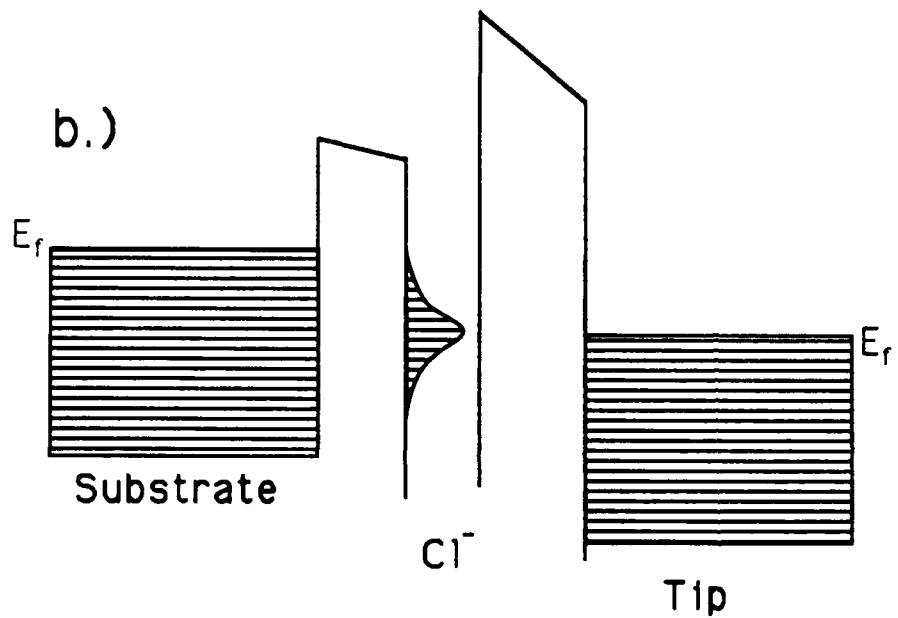
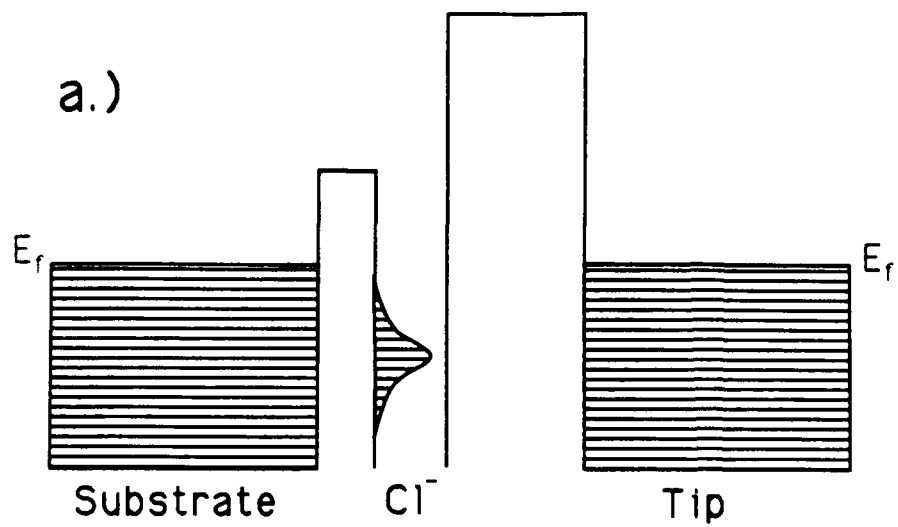
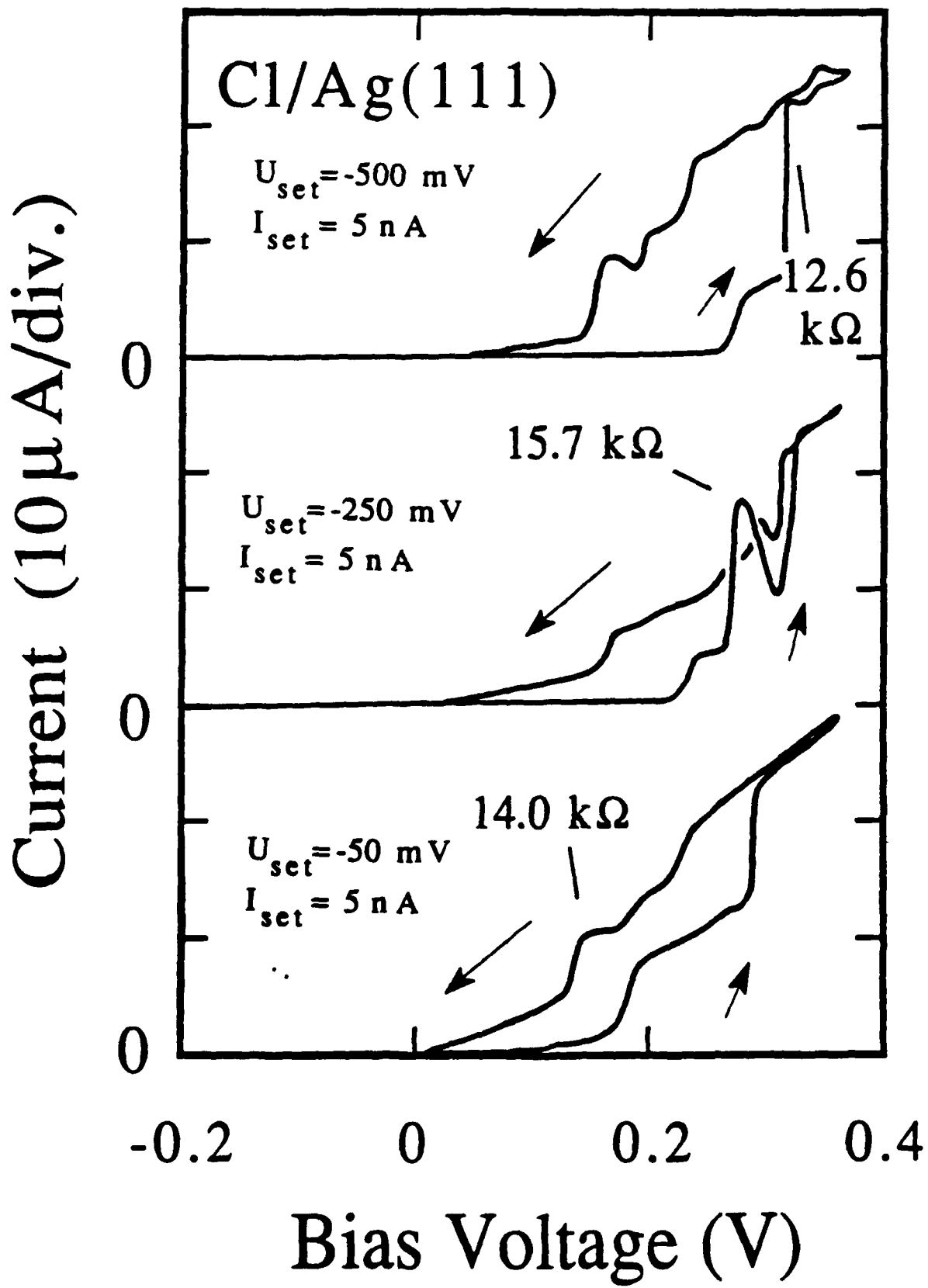


Fig. 16





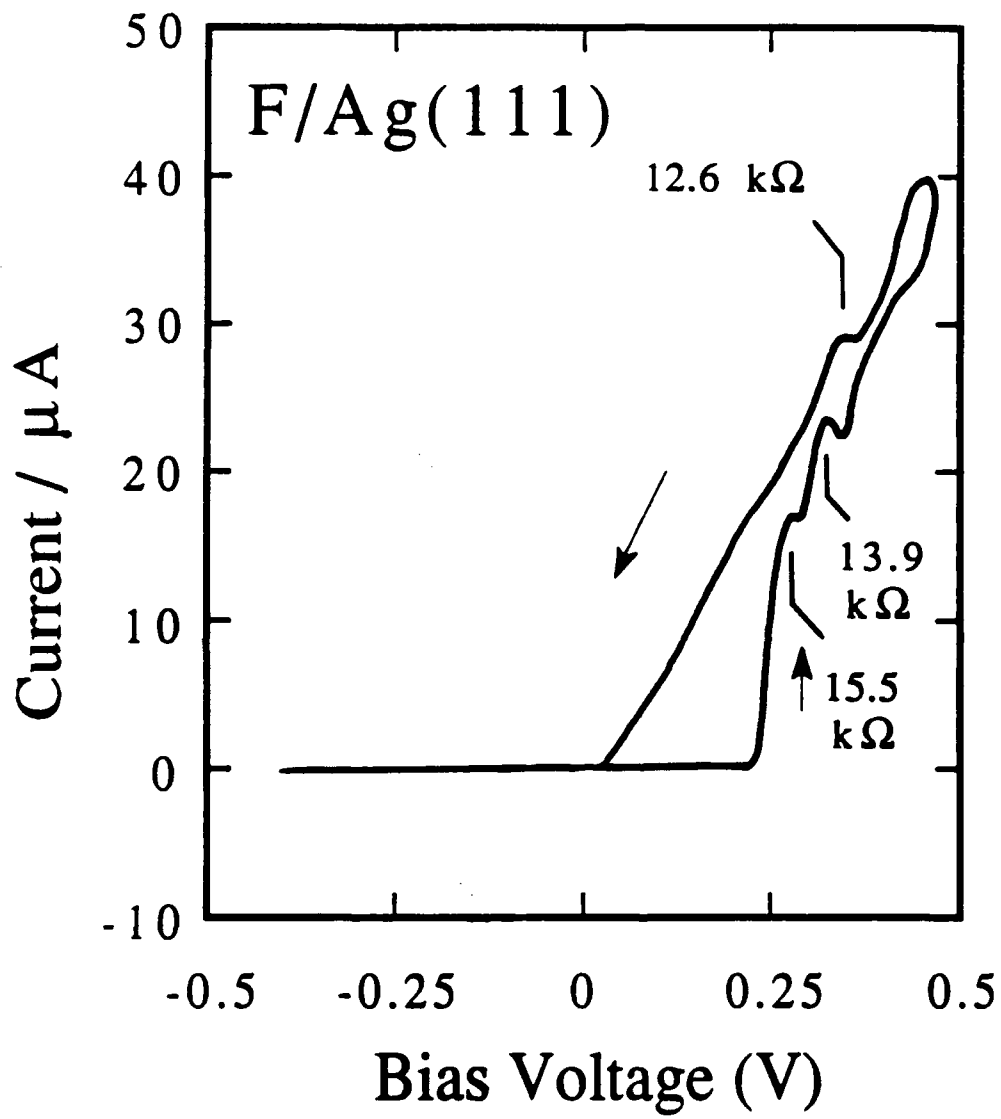


Fig. 7