ULTRAMICROANALYSIS UTILIZING ELECTRON TUNNELING

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Abstract - The field emission microscope (FEM), the field ion microscope (FIM) and the scanning tunneling microscope (STM) are the high resolution microscopes utilizing electron tunneling. Field emission electron spectroscopy (FEES), the atom-probe (A-P) and scanning tunneling spectroscopy (STS) were developed from FEM, FIM and STM, respectively. The atomic arrangement, composition and electronic states of the Si micro-cluster on a Mo surface and the atomic step on the Si(001) plane were investigated at the level of individual surface atoms.

Keywords: electron tunneling, ultramicroanalysis, field emission electron spectroscopy (FEES), atom-probe (A-P), scanning tunneling microscope (STM), scanning tunneling spectroscopy (STS).

The first ultra-high resolution microscope realized by utilizing electron tunneling is the field emission microscope (FEM) [1] which is the precursor of the field ion microscope (FIM) with atomically high resolution [2, 3]. The FEM study was extended to the field emission electron spectroscopy (FEES) [4, 5]. The FIM was combined with a mass spectrometer to mass analyze individual surface atoms and the combined instrument was named as the atom-probe (A-P) [6, 7]. While FEM and FIM observations are limited to the apexes of sharp tips, the scanning tunneling microscope (STM) [8, 9] has introduced high resolution microscopy for flat surfaces by passing tunneling current between a single apex atom of a scanning tip and an atom on a specimen surface. The STM study is extended to electron spectroscopy, scanning tunneling spectroscopy (STS) [10, 11], and the electronic states of individual surface atoms have been investigated.

APPARATUS

A-P/FEES The FEM and FIM have an identical simple structure consisting of a sharp tip and a screen in a vacuum chamber. When a negative high voltage is applied to the tip, the microscope serves as an FEM and the electrons field emitted from the tip apex project an enlarged image on the screen reflecting the local work function of the apex hemisphere which can be obtained by measuring the variation of emission current with applied tip voltage. When inert gas is introduced to the chamber and a positive high voltage is applied to the tip, the FEM functions as an FIM. The introduced gas atoms are field ionized above individual surface atoms of the tip apex. The positively ionized gas ions are repelled by the tip at a positive voltage and project a high resolution image showing the atomic arrangement of the apex.

The field emitted electrons can be energy analyzed by installing a Faraday cage behind the probe hole at the center of the screen, Fig. 1. The energy analyzer is the retarding field type and a negative potential as high as the tip potential is applied to the collector [12]. The electrons of deeper energy levels of the tip enter the collector as the collector potential shifts positively. An operational amplifier was directly attached to the collector of the Faraday cage because the incident current is extremely small. The high feedback resistor 10 MΩ generates the output voltage of 1 mV for the input current of 1 pA. Negative high voltages applied to the collector are isolated by an isolation amplifier. Tip and collector voltages are controlled by a computer and modulated by a sine wave generator, the
frequency 800 Hz and the amplitude 18 mVp-p. A lock-in amplifier is used to lower the noise level and to detect the modulation current signal which corresponds to the surface state density and the tunneling probability of the tip apex at the energy level near the Fermi level of the collector. The energy spectrum of the field emitted electrons is obtained by measuring the output signal from the lock-in amplifier as a function of the tip-collector voltage difference. The current passing through the probe hole is about 30 pA. Thus the time to measure a current for each voltage difference is as long as 1.6 sec and the acquisition time of an energy spectrum depends on the number of measuring points and is usually a few minutes. The energy resolution of this analyzer is approximately 70 mV.[5,13] The ions field evaporated from the apex also pass the probe hole and enter the flight space of the time-of-flight mass analyzer of the A-P, Fig. 1.

STM/STS An STM is installed in an vacuum chamber of 1-2x10⁻¹² Torr. The chamber is mounted on a vibration isolation bench and is equipped with a screen to project FEM and FIM images to examine the tip apex, a vacuum lock to introduce tips and specimens into the chamber and two stages for holding, heating and inspecting tips and specimens, Fig. 2.

Fig. 1. Schematic diagram of A-P/FEES. The tip and screen in the vacuum chamber form FEM/FIM. Field evaporated positive ions fly into the flight space after passing the probe hole at the center of the screen. For FEES the electron collector is inserted behind the probe hole.

Fig. 2. Schematic diagram of the STM vacuum chamber on a vibration isolation bench. The screen to project FEM and FIM images, a vacuum lock and two stages to heat and reserve tips and specimens are shown. The STM unit of a tip, a sample and a piezo tripod is mounted on a metal stack.
Scanning tips are prepared by electrochemically etching a [111]-oriented fine tungsten crystal wire to a sharp tip with an apex radius of less than 200Å because the apex atoms on the (111) plane are very stable and the tips can be resharpened to an apex with a single atom by simply heating it [14]. The tips are cleaned by heating in the STM chamber and the tip profiles are examined by observing FEM or FIM images.

Two STS modes are employed to study the electronic states of individual surface atoms: dual-polarity tunneling imaging (DPTI) [10,15] and current imaging tunneling spectroscopy (CITS) [11,16]. In DPTI a tip scans over a specimen surface keeping the tunneling current constant mode and each scanning line is scanned twice successively switching the specimen bias voltage from a positive voltage, for example 2V, to a negative voltage, -2V, and vice versa. In CITS, the tip scans from a pixel to another, keeping the current constant and a current-voltage (I-V) curve is obtained sweeping the sample voltage 128 steps from a positive voltage to a negative voltage at each pixel, for example from 3V to -3V, while fixing the tip-specimen separation, Fig. 3. One frame of the CITS image consists of 64x64 pixels and it takes \~90 s to acquire \~1 MB of data. The \((dI/dV)/(dV/dI)\) plot against bias voltages corresponds to the electronic state density of a specimen surface.

RESULTS

A-P/FEES ANALYSIS OF Si/Mo Electronic structures and compositions of Si microclusters on a Mo substrate were investigated with the A-P/FEES[5]. Silicon was deposited on a Mo tip apex by evaporating Si in vacuum. The Si-covered Mo tip was examined by observing an FEM image. Randomly distributed bright spots were Si clusters, Fig. 4(a), and one of the bright spots was brought to the probe hole of the A-P. Then the field emission current from the cluster passed the probe hole and was analyzed by the FEES. After each FEES measurement, few Si atoms of the cluster were field evaporated and mass analyzed by the A-P. The FEES measurement and A-P analysis were repeated until the Mo substrate was exposed and the exposed Mo surface was inspected by the FIM to identify the crystal plane of the probed area, Fig. 4(b).

Fig. 4. FE and FI images of Si deposited Mo surface. (a) FE image of Si covered Mo surface. The bright spots are Si clusters. Imaged at -550V at room temperature. (b) FI image of Mo substrate. The numbers are the Miller indices of the crystal planes exposed on the apex hemisphere. The image indicates that the probed area is the Mo(013) plane. Imaged at 6.59 kV with Ne at 1.0X10^-4 Torr and 50K.
The A-P analysis clearly indicates that the Si-Mo interface of a non-heated Si/Mo tip is atomically abrupt because the detected ions suddenly switch from Si to Mo as shown in Fig. 5. Since the number of atoms per one atomic layer in the probed area is usually 10 to 20, the Si coverage at the probed cluster is about 1 to 2 atomic layers. The FEES spectrum at a of Fig. 5 shows an energy gap and two peaks, $P_v$ and $P_s$, corresponding to the surface state and the valence band, respectively, and are characteristic of a semiconductive material implying that even a small Si cluster exhibits the properties of bulk silicon, Fig. 6(a). A similar energy gap was observed by the STM study of the Au surface covered by a cluster of 10 Si atoms[26]. The work function of a Si/Mo surface is found to be 10 to 20% higher than that of the clean Mo surface.

As Si atoms field evaporate, the Si cluster shrinks and $P_v$ diminishes and the energy gap narrows, Fig. 6(b). But even at C of Fig. 5, a shoulder corresponding to $P_v$ is seen on the metallic FEES spectrum, Fig. 6(c). The FEES spectrum of the Mo substrate Mo is metallic and the total emission current $I_{CT}$ increases significantly because the work function is lower than the Si cluster, Fig. 6(d). Heating a Si/Mo tip results in the formation of metallic Mo silicides. The A-P analysis of the silicide indicates that the average composition of the silicide formed by heating a Si/Mo tip at 600°C for 5 min is $M_o_3 Si$ and local compositions vary alternately between $M_o_3 Si$ and $M_o_3 Si_5$ which are 2 to 3 atomic layers thick. The silicide-Mo interface is also found to be atomically abrupt, Fig. 7. The FEES spectrum of the silicide is metallic, Fig. 8, and its work function is about 10% smaller than that of the Mo substrate. The observed low work functions of the silicide could be due to the difference in the binding states because the number of the Si-Si bonds per Si atom in Si clusters is much larger than that of the Si atoms in a silicide.
STM/STS OF Si STEP

The STM successfully depicted the atomic configurations of the single and double layer steps on the Si(001) plane[18,19] and the step bunches on the vicinal Si(111) plane[20]. Observed configurations of the single and double steps on the Si(001) plane were found to well agree with the energetically favorable configurations proposed by Chadi[21]. Hereupon the step configurations and the electronic states of the Si atoms at the step edge on the Si(001) surfaces were examined utilizing STM/STS.

Silicon specimens were prepared by heating the flat Si(OO1) surfaces at 1200-1300°C for 15 sec to 1 min and cooled at the rate of 3°C per sec. The heating was repeated several times until the surface was thoroughly cleaned and vicinal facets were observed.

The I-V spectra were obtained by the CITS method[16] and were numerically differentiated to acquire the (dI/dV)/(I/V) spectra. The tunneling spectra at sites A, B, C, D and A' along the line crossing the single step on the Si(001) plane, Fig. 9, are shown in Fig. 10. According to the Chadi's notation, the step in Fig. 9 is the S₃ step because the direction of the dimerized Si atoms on an upper terrace is normal to the step edge. Site A is located at the center of a dimer and site B is at the flip-down Si atom of the buckled dimer at the step edge of the upper terrace. The location of the flip-up atom at the edge of the upper terrace is denoted as C and that of the center of the dimer closest to the step edge on the lower terrace is D. Site A' is two dimers away from site D. Since sites A and A' are fairly away from the step edge, the conductance spectra are very similar exhibiting the gentle peaks at 0.6, -0.6, -1.4, -1.7, -2.1 and -2.4V. While the flip-down atom at site B does not show the peak at -1.7V clearly, the peaks at -1.4 and -1.7V are very sharp at sites C and D. No significant difference is noticed for the peak profile of the empty states above 0.6V.

The surface band gap indicated by the two peaks at 0.6 and -0.6V is comparable to those reported by the ultraviolet photo-electron spectroscopy study(UPS)[22] and the STM study[23]. Although the peak at 0.6V agrees well with the theoretically obtained value[24], the reported energy levels by UPS, 0.3 and -0.7 eV, and by STM, 0.3 and -0.8 eV, are slightly off from the present peak positions. The observed discrepancy could be due to the shift of the Fermi level by surface defects[25].

The I/V curves showed a steep increase at the bias voltage lower than -2.0V. This increase could be explained as the result of the enhanced field strength at the step edge[26]. However, the high peaks around -1.7V cannot be simply explained by the field effect because the (dI/dV)/(I/V) spectrum is not affected by the variation of the tunneling probability. Another explanation could be the charge build-up at these levels and/or the preferential tunneling through an unpaired dangling bond oriented to the apex atom of the tip above site D from the Si atom at site C as observed for a TiC crystal by the impact collision ion scattering spectroscopy[27].

CONCLUSIONS

Present study clearly demonstrates that the high resolution microscopies and spectroscopies utilizing electron tunneling are indispensably useful for the microanalysis of surface structures, composition and electronic states. Accordingly the development of a combined instrument of A-P/FEES and STM/STS is in progress to realize a new comprehensive analyzing technique.
Fig. 9. STM image and surface corrugation of the Si(001) plane across the $S_x$ step from A to A'. The vertical scale of the corrugation is about 30% larger than the line drawing. Imaged applying -1.0V to the sample and passing the tunnel current 0.2 nA.

Fig. 10. Tunneling spectra at positions at A, A', B, C and D of Fig. 9.

REFERENCES