

Invited**Atom-Probe and Scanning Tunneling Microscope Studies of Surfaces and Interfaces**

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Al-Ga exchange reaction at the Al-GaAs interfaces, oxidation processes and dopant distributions in the conducting polymer, polypyrrole, the atomically abrupt polymorphic boundary in barium titanate, and non-uniform composition in high temperature superconducting Y-Ba-Cu-O ceramics were investigated utilizing the unique capability of the atom-probe, atom-by-atom mass analysis. The A-P study suggests that the combination of the A-P and a scanning tunneling microscope (STM) is highly promising for clarifying a modulated surface structure with an minutely short range order.

1. Introduction

The atom-probe (A-P)¹⁻³⁾ is a combined instrument of a field ion microscope (FIM)⁴⁾ and a mass analyzer and can analyze the individual surface atoms observed by the FIM. The unique capability of this instrument has been successfully demonstrated by clarifying the structures and compositions of metal surfaces and metal-metal interfaces⁵⁾. Recently the introduction of the pulsed-laser A-P has opened a new A-P research area because it makes us possible to mass analyze highly resistive materials. Thus, this paper reports the results obtained by analyzing surfaces and interfaces of semiconductors, polymers and ceramics.

The unique feature of the scanning tunneling microscope (STM)⁶⁾ is the direct depiction of the local electronic states at the atomically high resolution and the charge distributions of Si and GaAs surfaces have been clearly illustrated in full color⁷⁾. However, no detailed study has been conducted on the surface with highly modulated structures in a very short range because the STM does not provide local compositions. Recently it has been realized that the combination of the A-P

and STM may lead to a new approach to investigate the electronic states of surfaces with modulated structures and compositions.

2. Principles and Structures of A-P

A specimen of the A-P is a sharp needle with a tip radius of less than 1000 Å. A high voltage applied to the tip exerts an extremely high field above the tip apex and the field ionizes the imaging gas atoms such as He and Ne. Then, the gas ions fly to the screen and project an FIM image.

Surface atoms and adsorbed molecules are also evaporated as positive ions by the unique phenomenon called field evaporation⁴⁾. Since the evaporation field varies with temperature and binding energy between surface and substrate atoms, the binding states of surface atoms and adsorbed molecules can be studied by examining the evaporation field. Furthermore, field evaporation proceeds orderly atomic layer-by-layer. Thus the sequence of evaporated ions gives the depth profile of composition with atomic resolution. Accordingly, the A-P, the combined instrument of an FIM and a mass analyzer with the detection sensitivity of a single ion, was introduced. Figure 1 is a

schematic diagram of the newly developed A-P with straight and electrostatically deflecting flight paths⁸⁾. The screen to project an FIM image has a probe hole of a few mm in diameter at its center. The area on the tip apex corresponding to the hole is a few Å to several Å in diameter. The evaporated ions pass through the hole and enter the flight path of the mass analyzer and then are detected one-by-one. In order to measure the flight time of each ion accurately, the moment of evaporation is confined to a short period by applying a pulse voltage of a few ns width. However, such a pulse contains high frequency components and does not propagate through a semiconductor needle effectively. Thus a new technique has been introduced to promote field evaporation of a resistive material by irradiating a pulsed-laser beam to the specimen tip at a dc voltage^{9,10)}. The straight flight path of the A-P in Fig. 1 is to examine the energy distribution of the evaporated ions and the deflected flight path is for the high mass resolution analysis.

3. A-P Mass Analysis of Surfaces and Interfaces

The A-P analysis showed that the silicide formed on a Si-covered W tip has the composition of W_{Si_2} with the Clb structure¹¹⁾ and that the W_{Si_2}/W interface is atomically abrupt. FIM images indicate the epitaxial growth of the W silicide from the W basal planes where the lattice of the (001) plane of W_{Si_2} matches that

of the $W\{001\}$ planes.

The analysis also revealed that the compositions of epitaxially grown Ni silicides at the Ni/Si and Si/Ni interfaces varies from Ni_4Si to $NiSi_4$ but the silicides exhibited only cubic structures^{12,13)}.

The Al-Ga exchange reaction at the Al/GaAs interfaces at room temperature was investigated extensively¹⁴⁾. The reactivity at the interfaces was found to vary with dopants. The Al/Si-doped GaAs interface is most stable and the reaction is fairly active at the interfaces with non-doped and Zn-doped GaAs^{9,10)}. An unexpected finding is that GaAs heated at 800 K for 10 min forms an Al/GaAs interface as stable as the Al/Si-doped GaAs interface.

In the A-P analysis of the conductive polymer, polypyrrole(PP), the polymer field evaporates as fragment ions breaking weak bonds in the PP structure. The variation of composi-

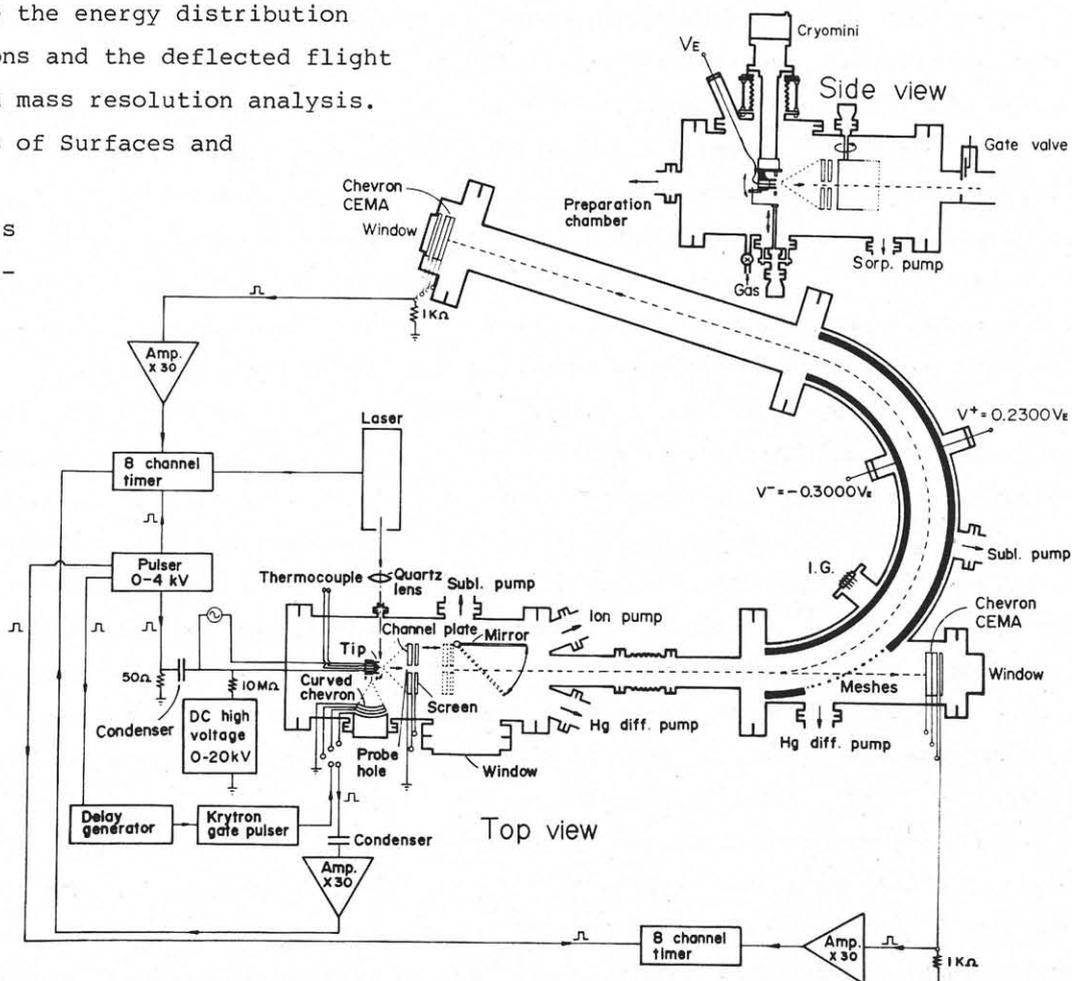


Fig. 1 Schematic diagram of the A-P.

tions due to oxidation and the role of oxygen in the metal-polymer bondings were investigated by analyzing the mass spectrum of fragment ions^{15,16}.

The conductive ceramics, barium titanate, was analyzed. An interesting finding is the abrupt change in the fragment ions evaporated from the ceramics while no change in its composition is noticed. For example, the detection of Ba^+ and TiO_2^{3+} are suddenly terminated and BaO^+ and Ti_2O^{3+} are detected as shown in Fig. 2. The observed abrupt change in ion species can be attributed to the phase boundary with different binding states.

The analysis of high temperature superconducting Y-Ba-Cu-O ceramics indicates that the ceramics composition varies significantly in a short range of a few tens Å, Fig. 3. Mass spectrum of detected ions indicates that Y atoms were found mostly as YO^+ , $YCuo^+$ and $YCuo_8^{2+}$. Few BaO^+ ions were detected, Fig. 4.

4. Principles and Resolutions of STM

When a sharp tip approaches a specimen surface within 10 Å, a tunneling current flows between them. Since the current changes sharply with the tip-to-surface distance, the tip scanning over the surface at a constant tunneling current shifts up and down following the surface corrugation. Thus the traces of tip motion correspond to the surface topograph.

The resolution of the image is higher than 0.1 Å in the vertical direction to the surface. In the lateral direction the resolution is 1.4 Å for Si and graphite and ~3 Å for metals⁷). Since the tunneling current flows through any insulating layer, the STM can be operated even in air and liquid.

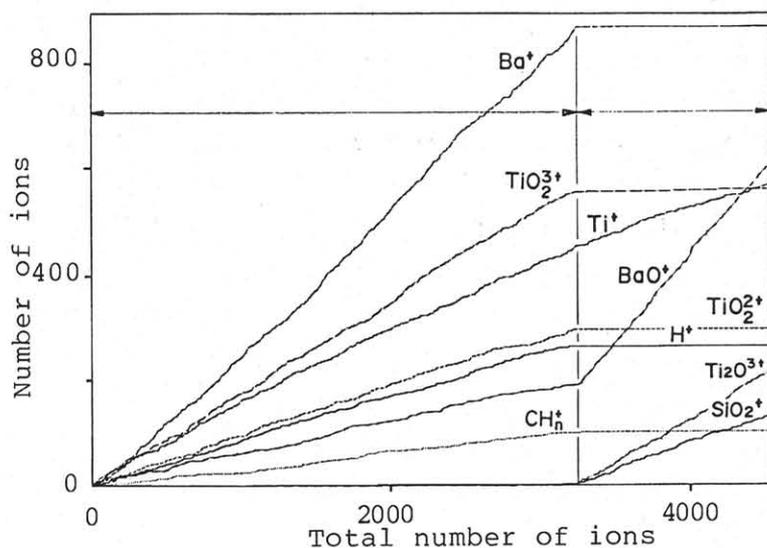


Fig. 2 Detection sequence of ions from barium titanate. The vertical line indicates the polymorphic boundary where detected ion species change.

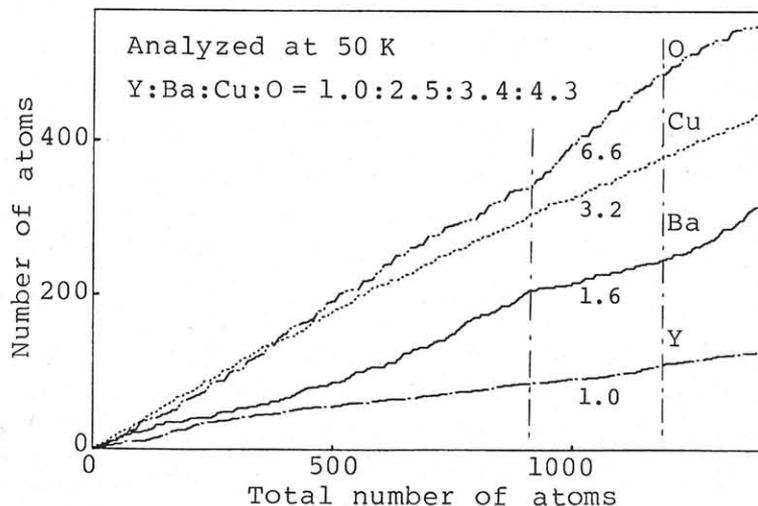


Fig. 3 Variation of the ceramics composition with depth. The local composition between two vertical lines is different from the average composition indicated in the figure. Where the concentration of Ba is low, that of O is high. The analyzed area is deepened about 1 Å by the detection of 10 - 20 atoms.

5. Current-Imaging-Tunneling Spectroscopy

Recently Hamers et al. mapped out the electronic states of the Si surface with a lateral resolution of 3 Å by the new method called Current-Imaging-Tunneling Spectroscopy (CITS)¹⁷. In this method the tip position is held stationary for a fraction of 1ms and the tunneling current is measured at various bias

voltage. By repeating this I-V measurement at each point along the raster scan, geometric structure of a surface and the spacial distribution of surface states are visualized⁷⁾.

6. Combination of A-P and STM

Although CITS is a highly powerful technique to visualize surface states, it requires to know the local composition of a specimen surface having modulated structures and compositions such as alloys, ceramics and polymers because the I-V characteristics strongly depends on the structures and compositions of the tip and specimen.

One possible way to map the variation of the surface states due to the structure modulation is to combine the unique capabilities of the A-P and STM. In the combined instrument of the A-P and STM a tip material having the modulated structures is A-P analyzed repeatedly. The specimen has a known homogeneous compositions such as a metal and the I-V curves are obtained for various tip compositions. After knowing the relation between the local tip compositions and the I-V curves, the tip and specimen materials are exchanged to obtain the current image of the specimen surface with modulated structures.

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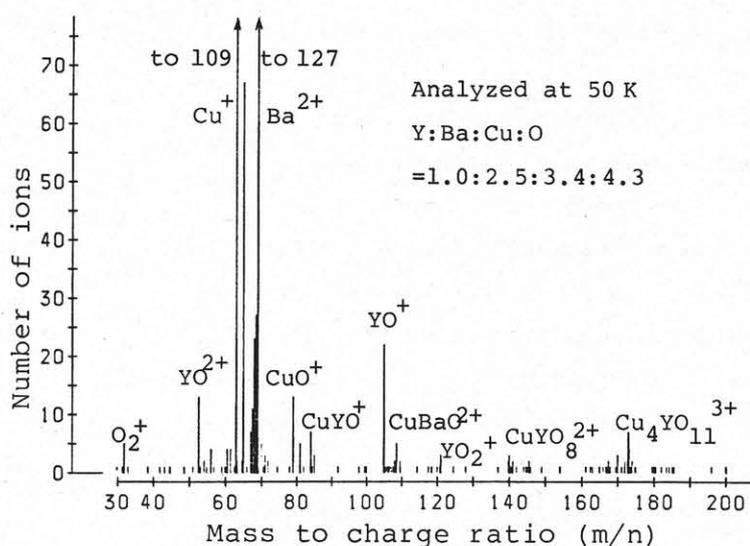


Fig. 4 Mass spectrum of ions detected by A-P analyzing superconducting ceramics. The numbers of atoms in Fig. 3 are plotted by counting the atoms in each ions of this figure in the detection order.

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