ELSEVIER

Journal of Alloys and Compounds 293–295 (1999) 361–363

Journal of ALLOYS AND COMPOUNDS

A new method for two-dimensional hydrogen analysis and its application to metal surfaces

Kazuyuki Ueda*, Ken'ichi Ishikawa, Masamichi Yoshimura

Toyota Technological Institute, Hisakata 2-Chome, Tempaku, Nagoya 468-8511, Japan

Abstract

A new technique for the analysis of the two-dimensional hydrogen distribution on a solid surface using electron-stimulated desorption (ESD) is described. The hydrogen distribution is observed as a two-dimensional histogram of the yield of desorbed hydrogen ions at scanning positions on the sample surface. We show a scanning ESD H^+ image of Cu 600-mesh at a magnification of 2000. The lateral resolution is estimated to be less than 1 μm from the ESD image obtained at the primary electron energy of 600 eV. As a demonstration of the scanning ESD, a hydrogen-terminated Si(100) surface was lithographed by a continuous electron beam before imaging. The linewidth and amount of desorption in the lithographed area depend on the electron dose.

Keywords: Time-of-flight mass spectroscopy; Electron-stimulated desorption; Scanning probe microscopy; Hydrogen

1. Introduction

When a solid surface is irradiated by slow electrons with energy below 1 keV, light ions are effectively desorbed as a result of electronic excitations. Electron-stimulated desorption (ESD) is useful to investigate the adsorbed hydrogen on metal surfaces [1]. A model mechanism of ESD of adsorbates on metal surfaces has been proposed by Menzel and Gomer [2] and Redhead [3]. This model is based on the dissociation mechanism of isolated molecules via a Franck–Condon transition to a repulsive neutral or ion excited state. Compared with other surface analytical methods for hydrogen detection on solid surfaces, such as Fourier transform infrared (FT-IR) [4], high-resolution electron energy loss spectroscopy (HREELS) [5], or elastic recoil detection analysis (ERDA) [6,7], ESD is very sensitive to the presence of hydrogen. Measurements of the ESD provide various information on the interaction between hydrogen and surfaces, for example the kinetic energy of desorbed ions and the threshold electron energy of desorption depend on the bonding energy of the species.

The yield of desorbed hydrogen ions is generally proportional to the amount of hydrogen in the probing area. Thus, the hydrogen distribution can be obtained by scanning of a fine-focused electron beam over the sample surface. It has been reported by Dylla et al. [8,9] that scanning ESD is useful for analyzing the hydrogen distribution on surfaces. But their scanning ESD image is inferior in lateral resolution using a continuous electron beam with high primary electron energy (2 keV) because of the low detection efficiency of their system. To obtain a large detection efficiency to analyze a very small probing area, we have used a time-of-flight (TOF)-type mass analyzer using a pulsed electron beam. The high detection efficiency of the TOF-type mass analyzer is due to the large solid angle for detection [10]. TOF-ESD also has the advantage that it can be combined with several other surface analytical methods in situ, such as low energy electron diffraction (LEED), Auger electron spectroscopy (AES), ESD ion angular distribution (ESDIAD), scanning electron microscopy (SEM), etc.

In the present paper we describe the characteristics and the applicability of the scanning ESD system newly developed in our laboratory. We discuss the lateral resolution of the system from a scanning ESD image obtained from a Cu 600-mesh. We also show the result of lithography on a hydrogen-terminated silicon surface by a continuous electron beam.

2. Experimental

The TOF-type mass analyzer and ESD measurement system were developed in our laboratory and applied to

*Corresponding author. Tel.: +81-52-809-1850; fax: +81-52-809-1853.

E-mail address: ueda@toyota-ti.ac.jp (K. Ueda)

0925-8388/99/$ – see front matter
PII: S0925-8388(99)00402-8

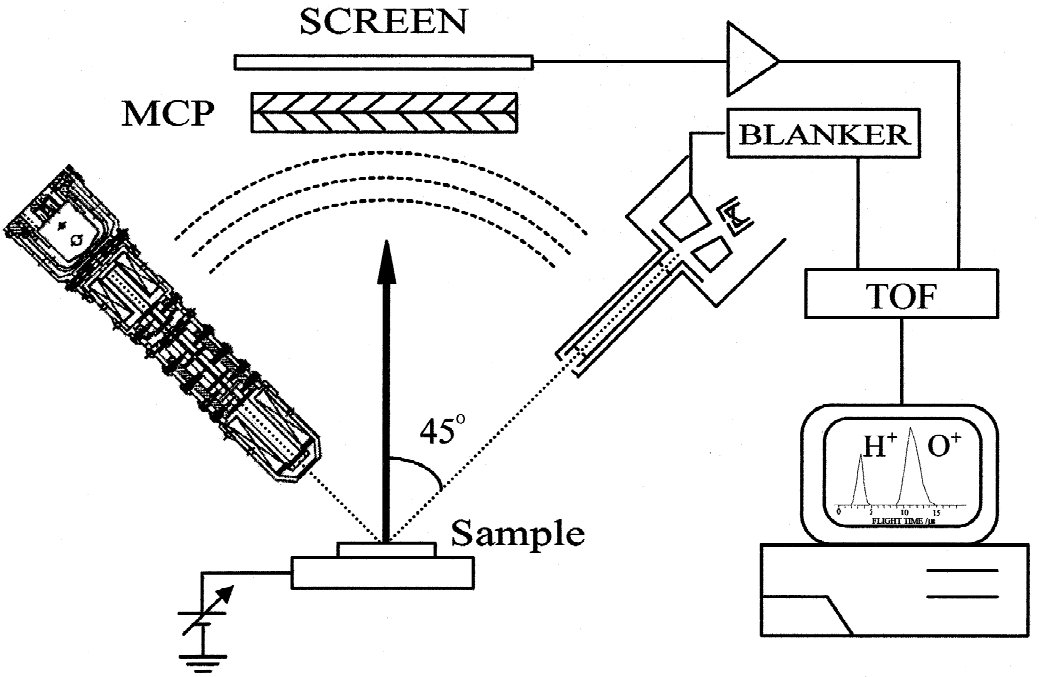

Fig. 1. Schematic drawing of the scanning ESD system for two-dimensional hydrogen analysis.

imaging the hydrogen distribution on solid surfaces. The experimental apparatus is shown schematically in Fig. 1. Details of the TOF-ESD and scanning ESD system have been reported elsewhere [10,11]. All experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 2.0×10^{-8} Pa. The UHV chamber is equipped with an off-axis-type electron gun, pencil-type electron gun, and TOF-type mass analyzer.

The off-axis electron gun (spot size 100 μm) is used for LEED, AES, ESDIAD, and ESD spectroscopy. A continuous beam was used for LEED, AES, and ESDIAD measurements, while a pulsed electron beam was used for TOF-ESD measurements. The pencil-type electron gun was originally designed for SEM with a spot size of 10 nm at a primary electron energy of 2 keV. It is possible to pulse the fine-focused electron beam with the primary electron energy below 800 eV and use it for two-dimensional ESD measurements. The incident angle of the electron beam is 45° with respect to the surface normal of the specimen. The duration of the pulses is 150 ns for the off-axis LEED gun and 220 ns for the pencil-type SEM gun. The repetition cycle of the pulsed electron beam is about 4 kHz on average.

The TOF-type mass analyzer consists of a three-grid mesh, microchannel plates (MCPs), and a fluorescent screen. The mass analyzer is positioned to the surface normal of the specimen, and the effective flight length of desorbed ions is 112 mm. Desorbed ions are accelerated to the mass analyzer by a positive sample bias. The yield of desorbed ions is accumulated for 10 000 electron pulses and stored in the memory of a personal computer.

3. Results and discussion

Firstly, we show an image of H^+ ions desorbed from a Cu 600-mesh as a demonstration of our scanning ESD system. A SEM image and a scanning ESD image in 64×64 pixels are shown in Fig. 2a,b, respectively. The magnification of the image is 2000. Both images were acquired using the primary electron energy of 600 eV. The brighter part represents the higher density of hydrogen on the sample surface. The ESD H^+ yield from adsorbed hydrogen on the Cu mesh makes a clear lattice image of the mesh (Fig. 2b). Since the periodicity of the lattice of the 600-mesh is about 42.3 μm, the lateral resolution of the scanning ESD system is considered to be less than 1 μm.

Next we present the results obtained from a hydrogen-terminated silicon surface. Fig. 3 shows an image of three lithographed lines on the H/Si(100) surface. The Si(100) sample was cleaned ultrasonically in acetone and subsequently dipped in buffered HF solution prior to evacuation to UHV. The sample was heated to outgas and cleaned by repeated flashing at 1200°C for 30 s below 1×10^{-7} Pa. In order to terminate the Si surface by atomic hydrogen, the sample surface was exposed to hydrogen near a hot W filament at 6.5×10^{-4} Pa for 17 min at room temperature. According to the ERDA result [7], the silicon surface was covered with about two monolayers of hydrogen. The lines were lithographed by a continuous electron beam with the primary electron energy of 800 eV at various line doses (current/scan speed) of (a) 935 nC/cm, (b) 2.80 μC/cm, and (c) 9.35 μC/cm. Lithographed areas are represented as

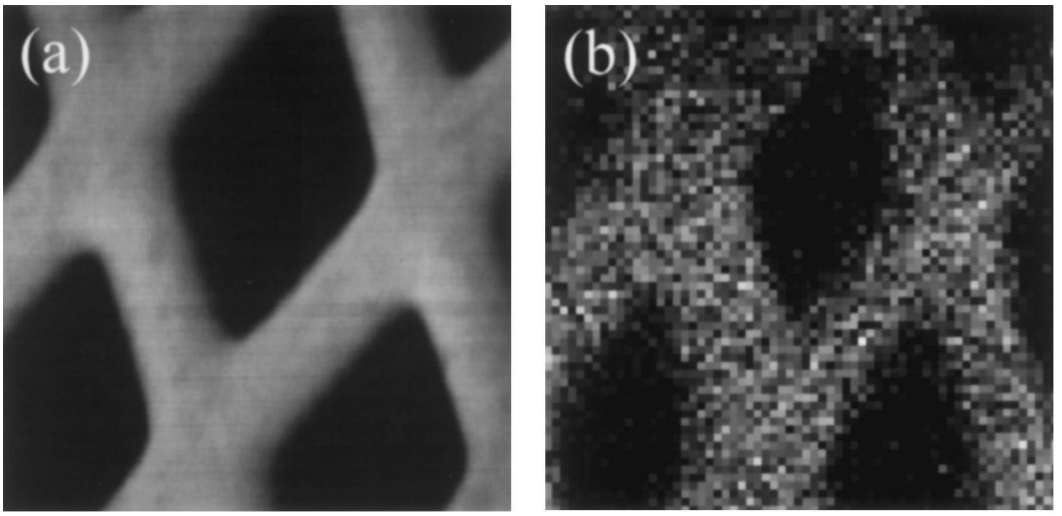

Fig. 2. SEM (a) and scanning ESD image in 64×64 pixels of H^+ ions desorbed from Cu 600-mesh (b). The primary electron energy was 600 eV. Magnification: 2000.

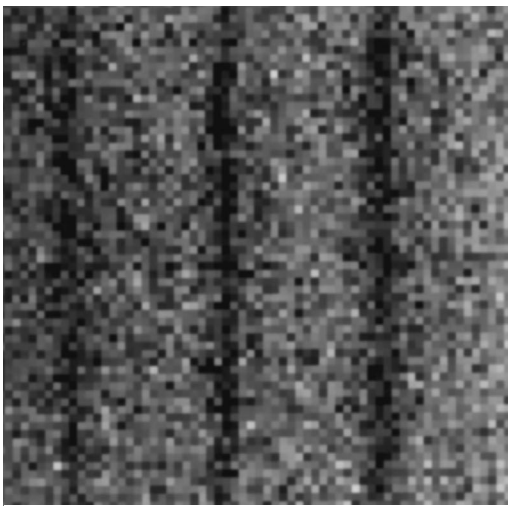

Fig. 3. Scanning ESD image of H^+ ions desorbed from a hydrogen-terminated Si(100) surface at various line doses of (a) 935 nC/cm, (b) 2.80 μC/cm, and (c) 9.35 μC/cm. The primary electron energy is 800 eV. The scanning area of the image is 128.6×164.3 μm^2.

dark lines in the scanning ESD image due to a smaller hydrogen concentration. The line becomes darker and broader with increasing electron dose. The amount of hydrogen in the lithographed area decreases exponentially with electron dose. The broadening of the linewidth is mainly attributed to scattering effects of primary electrons near the surface, because the threshold electron energy for hydrogen desorption is about 20 eV.

4. Summary

We have developed a new scanning ESD system combined with the TOF technique for analyzing the hydrogen distribution on solid surfaces. A clear image of the hydrogen distribution on a Cu 600-mesh has been obtained at a lateral resolution of less than 1 μm at the primary electron energy of 600 eV. Electron beam lithography was carried out on a hydrogen-terminated silicon surface at various electron doses, and the linewidth and hydrogen desorption on lithographed parts depend on the primary electron dose.

Acknowledgements

The authors thank Dr. Y. Sakai of Jeol Ltd. for his help with the development and improvement of the pencil-type SEM gun. This work was supported, in part, by a Grant-in-Aid for Scientific Research (B) (#10555010) on Priority Area A of ''New Protium Function'' from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] D. Menzel, Surf. Sci. 87 (1975) 370.
[2] D. Menzel, R. Gomer, J. Chem. Phys. 41 (1964) 3329.
[3] P.A. Redhead, Can. J. Phys. 42 (1964) 886.
[4] Y.J. Chabal, Surf. Sci. 168 (1986) 594.
[5] H. Kobayashi, K. Edamoto, M. Onchi, M. Nishijima, J. Chem. Phys. 78 (1983) 7429.
[6] R.J. Culbertson, L.C. Feldman, P.J. Silverman, R. Haight, J. Vac. Sci. Technol. 20 (1982) 868.
[7] K. Oura, J. Yamane, K. Umezawa, M. Naitoh, F. Shoji, T. Hanawa, Phys. Rev. B 41 (1990) 1200.
[8] H.F. Dylla, J.H. Abrams, C.T. Hovland, J.G. King, Nature 291 (1981) 401.
[9] H.F. Dylla, J.H. Abrams, Scann. Electron Microsc. III (1984) 1219.
[10] K. Ishikawa, M. Yoshimura, K. Ueda, Y. Sakai, Rev. Sci. Instr. 68 (1997) 4103.