Charge states of medium energy He ions scattered from single and poly-crystal surfaces

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Abstract

High-resolution medium energy ion scattering (MEIS) spectroscopy has unveiled fine structures of surfaces and interfaces. However, problematic issues arise due to its excellent energy resolution. In particular, when one uses He^+ beams, the He^+ fraction $\eta_+(1)$ for the scattering component from top-layer atoms is frequently non-equilibrated owing to short exit path length. This leads to significant uncertainties of the absolute amount of atoms located on top of a surface. To overcome this difficulty, it is essential to acquire reliable data of equilibrium and non-equilibrium charge fractions and also to model the charge exchange process based on a simple picture. In this paper, we analyze the MEIS spectra from single and poly crystals of Si, Ni and Cu together with c-axis oriented graphite and derive electron capture (σ_{10}) and loss (σ_{01}) cross sections dependent on emerging ion velocity. Here, we assume that a He ion when arrives at a Maffin-tin sphere after a large angle collision takes the He^+ state and then undergoes many charge exchanging collisions with valence electrons until leaving an electronic surface. The velocity dependent σ_{10} and σ_{01} values derived well reproduce equilibrium and non-equilibrium charge fractions of He^+ except for graphite and poly-crystal Si at relatively large emerging angles. Such a deviation comes from the markedly anisotropic distributions of the valence electrons of Si and graphite with strong covalent bonds.
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1. Introduction

High-resolution medium energy ion scattering (MEIS) spectroscopy has been utilized to determine surface and interface structures employing electro and magneto static energy analyzers [1–3]. In order to obtain absolute amounts of atoms located on top of a surface, the exact knowledge is indispensable of equilibrium and non-equilibrium charge fractions of He^+ and H^+ dependent on emerging velocity and angle. Up to now, however, there are only a few reports on non-equilibrium charge fractions of He ions [4–6]. According to our previous works, it was concluded that surface peaks originated from non-equilibrium charge state distributions appear only for low Z_2 materials ($Z_2 < 20$). However, recent MEIS experiments have revealed that such a surface peak also appears for single and poly crystals of Ni, Cu and Au at small exit angles of 20° and 35° (scaled from surface normal).

In this study, we measured the MEIS spectra for medium energy H^+ and He^+ ions scattered from single and poly crystals of Si, Ni and Cu together with c-axis oriented graphite. The surface peaks originated from non-equilibrium charge state distributions were observed for He^+ incidence but not for H^+ impact. We model the charge exchange process for He^+ incidence based on a simple picture, where it is assumed that a He ion when gets to a Maffin-tin sphere after a large angle collision takes the He^+ state and then undergoes many charge exchanging collisions with valence electrons until leaving an electronic surface. As a result, the electron capture (σ_{10}) and loss (σ_{01}) cross sections dependent on emerging ion velocity only were derived from the observed surface peaks originated from non-equilibrium charge fractions of He^+. The velocity dependent σ_{10} and σ_{01} values reproduce well the surface

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peaks observed at different emerging angles for poly and single crystals of Si, Ni and Cu and also for graphite.

2. Experiment

We used highly-oriented pyrolytic graphite (HOPG), poly-crystalline Si($\sim$2 nm)/SiO$_2$/Si(1 1 1) and Ni($\sim$10 nm)/SiO$_2$/Si(1 1 1) and single crystals of Ni(1 1 1) and Cu(1 1 1). The clean surfaces of Ni(1 1 1) and Cu(1 1 1) were obtained by repetition of sputtering by Ar$^+$ (0.75 keV) followed by annealing at 620 °C for 5 min in ultrahigh vacuum (UHV). Reflection high energy electron diffraction patterns showed sharp 1×1 patterns. In the case of graphite, stripping one monolayer with an adhesive tape and then annealing in UHV at 300 °C for 10 min led to a clean surface. The surface consists of small domains ($\sim$100 nm) with a c-axis oriented to surface normal. Poly crystals of Si and Ni films were deposited on oxidized Si(1 1 1) substrates at room temperature using Knudsen cells. The absolute amounts of Si and Ni were determined by Rutherford backscattering using 1.5 MeV He$^+$ beams. We confirmed no surface contaminations by Auger electron spectroscopy, MEIS and photoelectron spectroscopy. The samples were mounted on a six-axes goniometer.

A duoplasma ion source provides intense H$^+$ and He$^+$ beams with a low emittance. A well collimated beam was incident on a sample surface and the scattered H$^+$ and He$^+$ ions were detected with a toroidal electrostatic analyzer (ESA). A small beam size of 50 μm in the horizontal plane and a good spatial resolution of 50 μm of the position sensitive detector (PSD, PIAS: Hamamatsu Photonics) achieved an excellent energy resolution of 9×10^{-4}, which allows a layer-by-layer analysis. The detection efficiency (ε) of the PSD combined with three-stage micro-channel plates (MCP) was determined to be 0.52 ± 0.03 using a bakable surface-barrier-type solid state detector. The sample was positively biased by +90 V relative to the earth to collect secondary electrons and thus the integrated beam current was measured precisely within ±5%. In order to avoid radiation damage, the irradiated area was shifted slightly after an integrated beam current of 1 μC.

3. Results and discussion

The scattering yield from j-th layer atoms is expressed by

$$Y_j = Q(\mathrm{d}\sigma/\mathrm{d}\Omega)\Delta\Omega \cdot N\Delta x \cdot \varepsilon \cdot \eta_+(j) \cdot P_{CL}(j), \quad (1)$$

where Q, $(\mathrm{d}\sigma/\mathrm{d}\Omega)$, $\Delta\Omega$ and $\eta_+(j)$ are the number of incident ions, differential scattering cross section, the solid angle subtended by the toroidal ESA and He$^+$ (H$^+$) fraction for the scattering component from the j-th layer atoms, respectively. The hitting probability for the j-th layer atoms is denoted by $P_{CL}(j)$ and the areal density of an atomic layer by $N\Delta x$. For the poly-crystal targets and HOPG graphite, all the $P_{CL}(j)$ values are unity. To simulate MEIS spectra, we need the exact knowledge of stopping powers

and energy straggling. The stopping powers of poly crystals of Si and Ni were determined from observed MEIS spectra for Ni/SiO$_2$/Si(1 1 1) and Si/SiO$_2$/Si(1 1 1), because the absolute amounts of the stacked Ni and Si films were already known. In the case of graphite and single crystals of Ni(1 1 1) and Cu(1 1 1), the stopping powers and energy straggling were derived from the layer-resolved MEIS spectra. Fig. 1 shows the MEIS spectrum observed for 120 keV He$^+$ ions incident along the [1 0 0] axis of Cu(1 1 1) and backscattered to the [1 1 0] direction. The scattering components from the top- and second-layers are clearly resolved. For poly-crystal Si, we employed the energy straggling values calculated from the Lindhard–Scharff formula [7].

Fig. 2 shows the MEIS spectra observed for 80 keV and 120 keV He$^+$ ions incident on the poly-crystal Ni($\sim$10 nm) film varying emerging angle (scaled from surface normal). We can see that the surface peaks appear at small emerging angles. The best-fit (solid curves) was obtained by assuming larger He$^+$ fractions than the equilibrium ones for the scattering component from the top-layer. Here, the target is subdivided into thin layers with thickness of the areal density (1.86×10^{15} atoms/cm^2) of Ni(1 1 1). The He$^+$ fractions for the scattering component from top-layer Ni and Cu atoms $\eta_+(1)$ are plotted in Fig. 3 as a function of emerging angle for single crystals of Ni(1 1 1), NiO(0 0 1), NiSi$_2$(1 1 1) and Cu(1 1 1) and for poly-crystal Ni films. The scattering angle was fixed to 90° and the emerging velocity is 2.25–2.26×10^8 cm/s. Apparently, the $\eta_+(1)$ value increases with decreasing emerging angle and at emerging angle above 60° it reaches the equilibrium value of 0.42 predicted by Marion and Young [8].

In order to explain quantitatively the non-equilibrium He$^+$ fractions $\eta_+(1)$, we propose a simple model, as shown in Fig. 4. An electronic surface is expanded toward the vac-
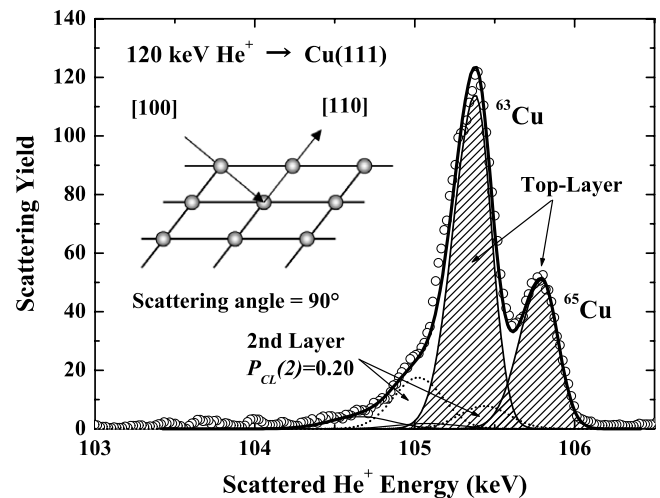

Fig. 1. MEIS spectrum observed for 120 keV He$^+$ ions incident along the [1 0 0] axis of Cu(1 1 1) and backscattered to the [1 1 0] direction. Solid curves are the best-fitted total (thick solid) and deconvoluted spectra from the top (shaded), second (dashed) and third layers (thin solid). The best-fit was obtained assuming the He$^+$ fraction to be 0.563 for the scattering component from the top-layer.