Ion bombardment of Ni(110) studied with inverse photoemission spectroscopy and low-energy electron diffraction

Benjamin Young [a,*], James Warner [b], David Heskett [b]

[a] Physical Sciences Department, Rhode Island College, 600 Mount Pleasant Ave., Providence, RI 02908, USA
[b] Department of Physics, University of Rhode Island, East Hall, 2 Lippitt Rd., Kingston, RI 02881, USA

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ABSTRACT

Inverse photoemission spectroscopy (IPES) performed on clean Ni(110) reveals an unoccupied electronic surface state with energy ~2.5 eV above the Fermi level for emission near the $\bar{Y}$ point of the Surface Brillouin Zone. Ion bombardment of the sample creates defects that reduce the intensity of the peak in IPES spectra. Sharp, intense diffraction spots in low-energy electron diffraction (LEED) patterns taken of the clean surface become dimmer after bombardment. Results of these measurements are compared to Monte Carlo simulations of the sputtering process to ascertain the approximate size of clean patches on the sample necessary to sustain the IPES and LEED features. At 170 K, the IPES surface state peak appears closely associated with the population of surface atomic sites contained in clean circular patches of about 50 atoms. The LEED patterns persist to greater degrees of sputtering and are associated with smaller clean patches. Both measurements performed at 300 K indicate significant self-annealing of the sputtering damage.

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1. Introduction

Surface electronic states on metals have been of interest since their observation by Gartland and Slagsvold [1] almost 40 years ago due to their roles in determining electronic and chemical properties of the surface and how they differ from bulk properties [2–6]. Also of interest, for fundamental understanding as well as for development of technologies on controlled systems which more closely approximate real-life surfaces, investigations into defects, and adsorbed species at surfaces have been studied extensively [7–14].

Ion bombardment, or sputtering, in itself is a topic of considerable importance. In addition to being the first step in many surface characterization techniques, sputtering can induce nanopatterning of surfaces and is a powerful tool for creating novel materials [13–18]. Additionally, low-energy sputtering may be considered as an inverted layer-by-layer growth (see [15] and references therein).

Morgenstern and coworkers [19] showed surface state depopulation through the disappearance of its characteristic signal in a scanning tunneling microscopy (STM)/spectroscopy (STS) study of Ag(111) for terraces less than 3.2 nm wide. Pons et al. [20] studied the effect of surface state confinement to monatomic step wells on the surface of Ni(111). In that work, the authors characterized differences in STM data due to the surface state expressed in triangular patches created by indenting the surface with the triangular STM tip (12.5 nm on a side). More recently, Ruggiero et al. [21] used STM to discover that

Cu$_2$N islands grown on Cu(100) support two surface states for large islands. One state disappeared on islands of less than ~50 atoms and the other persisted down to islands of 12 atoms.

While the size of nanostructures clearly plays a role in the intensity of surface states, temperature is also a factor. In reflection anisotropy spectroscopy (RAS) investigations of clean Cu(110) under low-energy noble gas ion bombardment, Martin et al. [22] witnessed significantly reduced intensity of the signal due to the ~2 eV surface state at the $\bar{Y}$ point for increasing sample temperatures, but Bremer et al. [18] observed no changes in its intensity for sputtering at room temperature. Heskett et al. [12] reported, through inverse photoemission spectroscopy (IPES) measurements, that although no change in the surface state intensity was observed for sputtering by 1 keV Ne + at room temperature, it decreased monotonically for similar sputtering at 170 K and suggested a room temperature self-annealing effect. Furthermore, through simulations of the sputtering process, they predicted that the existence of a well-defined surface state signal in the IPES spectra would require unsputtered square surface patches of about 150 atoms.

RAS experiments can simultaneously observe occupied and unoccupied surface states by measuring transitions between them, and this feature has prompted other explanations for quenching of the unoccupied surface state. Sun et al. have observed in multiple studies that the RAS signal indicating transitions between occupied and unoccupied surface states on Cu(110) was strongly attenuated by adsorbates and ascribed this to isotropic scattering-induced depolarization of the occupied state [23–25]. Martin and coworkers [26] observed a similar reduction in the RAS signal on Ni(110) after adsorption of CO and Na, and noted that the signal was sensitive to the specific sample cleaning

* Corresponding author. Tel.: +1 401 456 9644.
E-mail address: byoung@ric.edu (B. Young).

procedures before treatment with adsorbates. Furthermore, they identified a broader RAS signal for Ni(110) than was seen in earlier work on Cu(110). Recently, Isted *et al.* [27] investigated Cu(110) under ion bombardment at normal incidence with RAS, STM, and a version of the scattering model developed by Poelsema and Comsa [28]. In that study, the authors find close agreement between their integrated RAS signal intensity at various sputtering doses and the simulated fraction of surface cells not contained in circular patches of about 19 unit cells surrounding defects. This is supported by other studies [29,30] on the same system with adsorbates and a variety of defects where cells not within ~20 unit cell patches were proposed to support the measurement signal.

In this study, we present low-energy electron diffraction (LEED) and inverse photoemission investigations carried out at room temperature and 170 K on ion-bombarded Ni(110) to further elucidate the process of sputtering at low doses and to understand how sputtering modifies structural and electronic properties of the clean surface. We also compare these results to Monte Carlo simulations of a sputtered crystal to estimate the size of circular, unsputtered patches of the sample surface associated with the LEED and IPES features.

2. Experimental

All experiments were conducted in an ultra-high vacuum chamber with a base pressure ~7 × 10^{-11} Torr. The chamber is equipped with a home-built angle-resolved inverse photoemission spectrometer and Physical electronics' low-energy electron diffraction (LEED) system.

The clean Ni(110) surface was prepared by sputtering incident at 70° relative to the sample normal with 500 eV Ar + ions for 30 min at an Ar pressure of 5 × 10^{-5} Torr and an emission current of 20 mA, followed by annealing to 750 K for 5 min. The sample holder was constructed from tantalum foil folded around tungsten wires that are coupled to copper posts fed through a dewar, which could be filled with liquid nitrogen for cooling. Sample heating was accomplished by passing a high current through the wires that suspend the sample holder and was monitored by a type-K thermocouple spot-welded to the sample holder.

Ion bombardment of the sample for IPES and LEED measurements was performed by back-filling the chamber with high-purity argon to various pressures in the 10^{-7} or 10^{-6} Torr range, followed by sputtering with 500 eV ions at 70° off-normal incidence and 20 mA emission current. For sputtering at 300 K and 170 K, the bombardment-induced ion current measured between the sample and the ground was 0.23 and 0.035 μA cm^{-2}, respectively. The ion current dropped by less than 10% in all cases during sputtering and was recorded for use in the sputtering simulations.

2.1. LEED measurements

LEED measurements were performed immediately following each sputtering event, initiated as soon as the sputter gas had been evacuated and the chamber pressure recovered to below 2 × 10^{-10} Torr. For all measurements in this study, a 120 eV beam energy was used with an emission current of 1 mA, and the phosphor screen voltage was fixed at 5 keV. LEED images were acquired with a home-built CCD camera apparatus affixed to the viewport directly opposite the LEED screen.

Analysis software written in-house was used to analyze the LEED images using a procedure similar to Roučka *et al.*[31] and develop spot intensity profiles. Taking rough locations of the diffraction spots in the clean sample LEED pattern image as input from the user, the software is capable of correcting the spot center pixel values and tracking the slight variations of the centers through the whole progression of images. Once the centers are located, the software calculates data pairs of the average intensity value in each set of nearest neighbor pixels with the radius of the nearest neighbor set. The intensity of a given spot is then computed as the midpoint Reimann sum, above the background level, of the average pixel intensity vs. radius from the center pixel.

2.2. IPES measurements

Immediately following collection of the LEED images, inverse photoemission spectroscopy (IPES) measurements were performed. The IPES instrument is operated in isochromat mode and is comprised of an electron gun of the Erdman–Zipf design [32] to provide electrons over a range of incident energies and a Geiger–Müller tube to detect photons emitted from the crystal. The detector is filled with helium to 18 Torr (uncorrected pressure read by an N$_2$-calibrated Convectron gauge), before opening a valve to iodine crystals that are allowed to equilibrate. The entrance window of the detector is a 2.5 mm-thick SrF$_2$ disc with a diameter of 1". This arrangement permits detection of photons with 9.5 eV with a band-pass of approximately 0.5 eV as the difference between the photoionization threshold of iodine and the energy cutoff for transmission through the end window [33].

The detector signal was conditioned by a fast-pulse counting circuit, delay line amplifier, and single channel analyzer before being recorded as count rate vs. the energy of electrons incident on the sample from the electron gun. For all spectra taken in this study, the end window of the detector was positioned by a linear manipulator to within 2 cm of the sample surface at 45° relative to the sample normal. The electron gun was aimed 45° off the sample normal direction, which corresponds to the $\bar{Y}$ point of the Ni(110) Surface Brillouin Zone. The electron energies were scanned in steps of 100 meV and held for 250 ms before proceeding to the next energy step. The spectra collected for this study are sums of 50 scans, normalized to the average current developed on the sample at each energy step. IPES spectra of the clean sample showed no changes in feature intensities or locations over a period of a few hours.

2.3. Simulations

A clean 1000 × 1000 atom surface was modeled as an array of zeroes and array elements corresponding to Monte Carlo selected ion impact sites were incremented by one to simulate the sputtering process. To determine the number of ion collisions, we obtained an analytic expression for the ion flux from fits to the sample current data collected during sputtering, an estimation of the ratio of nickel sample area to the total current collection area by image analysis, and the area of the surface unit cell. From this, we obtained an average number of collisions per surface atom during an event by integrating over the time range of the event. We assumed each collision with the surface removed, on average, two atoms. This is supported by the conclusions of Vasylyev and co-workers in their study of low-energy Ar ion bombardment on low index nickel surfaces [34], where it was suggested that low-dose sputtering on this system likely produces vacancy point defects and adatoms with mean damage area per ion collision of about 5 unit cells. We note, however, that other authors have reported various higher estimates for the yield and damaged area per ion impact [27, 34,35].

For each collision in the simulation, 1–3 atoms were removed from the simulated crystal with equal probability. If one atom was chosen, only the primary atom was removed. If two or three atoms were removed, atoms adjacent to the primary location were also removed with probability based on the geometry of the Ni(110) surface unit cell. The simulated crystal was analyzed to determine the number of atomic sites in the crystal contained in unsputtered patches of radius *r*, where *r* was varied. The analysis was run over each subsequent sputtering increment to develop curves corresponding to each value of *r* to define f(θ)^r, the relative population of surface atoms in patches of unsputtered atomic radius r, as a function of θ (equivalent monolayers removed). We also calculated θ values for the IPES and LEED experiments.