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Angular, temperature, and impurity effects on secondary electron emission from Ni(110)

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The secondary electron emission from a temperature-controlled Ni(110) sample was examined for 50–1500 eV electrons impacting at 0°–35°, 50°, and 78°. Measurements showed a non-cosine dependence on an electron incidence angle: the yield has a maximum at 0°, minima at ±12°, and increases at larger angles up to 35°. This trend in angular dependence is characteristic of single crystal materials and is due to increased secondary electron generation when primary electrons are directed along a close-packed direction. For example, compared to polycrystalline nickel, the yield for Ni(110) from primary electrons at 0° (i.e., along the [110] direction) is up to 36% larger. Additionally, secondary electron yields are highly sensitive to incident electron energy (most notably between 0 and 500 eV) and to the presence of adsorbed carbon monoxide [with an up to 25% decrease compared to clean Ni(110)]. However, yields are independent of sample temperature between 300 and 600 K and of exposure to deuterium ions leading to formation of subsurface hydrogen. These results reaffirm the unique secondary electron emission properties of single crystals materials and highlight the importance of crystal orientation. Results are important for plasma-enhanced chemistry applications that utilize Ni(110) catalysts, since larger secondary electron emission may facilitate reactions of adsorbed species. Published by AIP Publishing.

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I. INTRODUCTION

Bombardment of materials by energetic ions, neutral atoms, and electrons can lead to the emission of secondary electrons from the materials. Secondary electron emission (SEE) is largest for incident electrons (i.e., primary electrons), where the total SEE yield (defined as the ratio of the emitted electron flux to the incident electron flux) can exceed unity.

These secondary electrons may be primary electrons that are elastically and inelastically reflected in the near-surface region of the material.1,2 However, for primary electron energies above a few tens of eV, the majority of the secondary electrons are true secondary electrons created within the material due to ionization and excitation of atoms by incident primary electrons.3–5 The generated true secondary electrons are emitted isotropically and may generate further true secondary electrons in cascade ionization and excitation collisions as they diffuse to the material surface; note that reflected primary electrons en route to the surface may also generate true secondary electrons. True secondary electrons that reach the surface with sufficient energy to overcome the material surface barrier may be emitted and are characterized by low emission energy (<50 eV). Therefore, true secondary electron emission occurs via a three-step process: (i) generation (affected by primary electron energy), (ii) diffusion to the surface (affected by primary electron energy and angle), and (iii) escape into vacuum (affected by surface adsorption and via the material work function).

SEE from plasma-facing materials can alter the sheath potential and adversely affect device performance and life,6 making it essential to maintain a low emitting surface. For example, textured materials with nm-to-mm sized grooves,7,8 pores,9 and fibers10–16 are being investigated due to their ability to recapture emitted electrons and thus for their low SEE properties. Nickel is currently used for electronics manufacturing and as catalysts for making carbon nanotubes via plasma-enhanced chemical vapor deposition.17,18 Both polycrystalline and single-crystal nickel have been proposed for the plasma-facing surface in tokamaks due to preferential trapping of helium.19 In such applications, SEE may lead to reduced plasma electron temperatures. Furthermore, SEE can affect chemical reactions occurring at metallic surfaces. For example, nickel is currently being investigated as a catalyst for plasma-enhanced dry reforming of methane (i.e., \( \text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{H}_2 + 2 \text{CO} \)). Of particular importance is Ni(110) for its unique ability to adsorb and dissociate CO\(_2\) below 200 K and under ultra-high vacuum conditions.20 For such applications, the low energy (~2–5 eV) secondary electrons emitted from the catalyst may contribute to further fragmentation of CO\(_2\) and CH\(_4\), as well as charging of nickel nanoparticles.

Previous authors have investigated SEE from clean polycrystalline Ni at room temperature.21–25 These authors

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compared their results to as-received Ni, likely covered with impurities and observed larger SEE from the more contaminated surfaces. Additionally, Rao investigated SEE from H2-exposed cryogenically cooled polycrystalline Ni and found that the total SEE yield increased by more than 50%.26 In contrast, little previous work has investigated SEE from nickel single crystals. Total SEE yields from Ni(110) in particular have only been measured for a clean surface at room temperature and for primary electrons at 50° and 78°.27 Yet, as was first discovered by Laponsky and Whetten28 and observed by others thereafter,29–38 SEE from single crystals may be significantly different from their polycrystalline counterparts due to electron interactions with the crystal lattice.

In this paper, we expand upon this earlier work by investigating the SEE from Ni(110) for a range of primary electron energies, primary electron angles, sample temperatures, and sample surface compositions that affect true secondary electron (1) generation, (2) transport, and (3) surface barrier. Total SEE yields for clean Ni(110) are presented for up to 1.5 keV, 0°–78°, and 300–600 K. Furthermore, total SEE yields of Ni(110) exposed to deuterium ions and to carbon monoxide residual gas are presented and compared to clean Ni(110). A description of the experiment used for SEE measurements is provided in Sec. II, and results of total SEE yield are presented in Sec. III. The paper concludes with suggestions on how to take advantage of SEE-enhanced surface chemistry.

II. EXPERIMENTAL SETUP

An ultra-high vacuum (<5 × 10−10 Torr) facility at the Princeton Plasma Physics Laboratory equipped with surface science diagnostics was used for the investigation of SEE (see Fig. 1). A 10 × 10 mm2 Ni(110) single crystal polished to a surface roughness of less than 0.01 μm was mounted between two tantalum posts by spot-welding to a 0.015-in. diameter tantalum wire. The sample was cleaned of sulfur impurities by sputtering with 1 keV argon ions from a tectra GenII electron cyclotron resonance (ECR) plasma source. The sample was then flashed to 1100 K by running current through the tantalum wires to remove any adsorbed C and O and to anneal the sample. Low Energy Electron Diffraction (LEED) using PHI 15-120 4-grid LEED optics was performed to obtain a diffraction pattern of the sample on the final phosphor-coated hemispherical screen, and thus to ensure that the sample was successfully annealed. The orientation of the crystal (e.g., the vertical/rotation axis corresponding to the [2 2 5] direction) was also deduced from the LEED pattern. A PHI 255G cylindrical mirror analyzer was used for Auger Electron Spectroscopy (AES) to monitor the surface elemental composition before and after SEE measurements.

SEE from Ni(110) under several conditions was investigated. The sample mount was attached to a rotary stage that allowed SEE to be measured at a range of primary electron incidence angles from 0° to ±78°. By continuously running current through the tantalum wires spot-welded to the sample, the sample may be kept at elevated temperatures during SEE measurements. The current was set with a Eurotherm 3508 PID controller, and the temperature was monitored using a type C thermocouple spot-welded to the back of the sample. Ni with subsurface hydrogen was prepared by exposing Ni(110) to 700 eV deuterium ions from a PHI 04-303A ion gun at 2 × 10−8 Torr for 150 s, while the sample was held at 250–280 K. After SEE measurements, the amount of adsorbed hydrogen was determined by using Temperature Programmed Desorption (TPD). During TPD, the sample was heated with a 10 K/s linear temperature ramp up to 650 K while monitoring the H2 (2 amu), HD (3 amu), and D2 (4 amu) signals with a UTI 100C Quadrupole Mass Spectrometer (QMS); the Eurotherm 3508 PID controller was again used for TPD measurements.

The AES spectra of clean and as-received Ni(110) after SEE measurements are plotted in Fig. 2. The AES spectra of clean Ni have large peaks at 61, 716, 782, and 848 eV and smaller peaks at 102, 663, 676, and 865 eV corresponding to Ni.39 The as-received Ni sample has additional peaks at 273, 381, and 510 eV, corresponding to C, N, and O, respectively. From the peak-to-peak heights of the C, N, O, and Ni peaks at 273, 381, 510, and 848 eV, respectively,33 and the AES sensitivity factors,40 the surface composition of the as-received sample was determined to be 78% Ni, 14% C, 5% N, and 3% O. No AES spectrum was recorded for the D2+-exposed sample since AES cannot detect hydrogen.

TPD spectra of H2, HD, and D2 desorbed from the D2+-exposed Ni(110) sample are plotted in Fig. 3(a). The D2 and
HD peaks at approximately 340 K and 440 K correspond to surface adsorbed hydrogen and subsurface hydrogen, respectively. By comparing the total area under the D₂ desorption curve after the D₂⁺ SEE measurements to the total area under the H₂ desorption curve after H₂ exposure leading to H₂ saturation, the sample was determined to have 55% of the hydrogen saturation [which is 1.5 monolayers for Ni(110)⁴²]; no D₂ was detected from the unexposed sample. Note that HD was likely formed due to isotope exchange with background H₂ and is larger at 340 K than 440 K due to a higher probability of D₂ undergoing isotope exchange at the surface. Figure 3(b) shows TPD spectra of Ni(110) that has allowed to sit in the chamber background for 40 min and 190 min after cleaning and that has been exposed to 3.3 L of CO (“Ni + CO”) and to CO leading to saturation (“Ni + CO saturation”); note that 1 L = 10⁻⁶ Torr s. CO peaks at 280 K and 430 K correspond to chemisorbed CO and are seen to increase with time after surface cleaning and with dosed CO. By comparing the total area under the 190 min curve to the area under the 3.3 L CO curve and under the CO saturation curve, it is estimated that 1.6 L (or less than 0.25 monolayers) of CO was adsorbed on the sample when sitting in the chamber background for 190 min.

Electron guns integral to the LEED optics and the AES system were used to produce primary electrons with energies up to 1500 and 3000 eV, respectively, for SEE measurements. Primary electron current IPE was measured on the sample while the sample was biased above +80 V to suppress SEE and ranged between 0.5 and 15 μA. Secondary electron current ISE was measured (1) on the sample when grounded or biased slightly negative [i.e., ISE = Isample(Vsample) - IPE with Vsample = -20 to 0 V] to minimize tertiary electrons from the chamber walls or LEED grids to the sample and (2) on the grids of the LEED optics when the first grid G1 was biased above +40 V [i.e., ISE = ILEED(VG1) with VG1 > 40 V] to increase the collection beyond the 120° solid angle of the LEED optics [see Fig. 1(b)]. From the primary and secondary electron currents, the total SEE yield σ = ISE/IPE was calculated. Note that secondary electron current was only measured with method (1) when using the AES electron gun, since the AES system has a very small collection solid angle. Additionally, secondary electron current was only measured with method (2) for actively heated samples since heating was accomplished by running current through the sample from an external power supply. A Keithley 2410 source meter was used to apply voltage and to measure current from the sample, while a Keithley 6485 picoammeter in parallel with a battery was used to measure current on the LEED optics. Measurements were performed repeatedly and error bars due to measurement repeatability, systematic error due to unsaturated primary/secondary currents when suppressing/inciting SEE, and instrumentation error from the Keithley electrometers are included in the plots below. See Refs. 5 and 43 for further details on the approach for measuring SEE, and Ref. 44 for details on the facility.

III. RESULTS AND DISCUSSION

Total SEE yields for clean Ni(110) at 0° and a range of primary electron energies are presented in Fig. 4(a) as a function of time after cleaning. At any given time, the total SEE yield initially increases with primary electron energy, then decreases for primary electron energies above approximately 600 eV. For example, at 0 min after cleaning, the yield increases by 41% between 180 and 580 eV, then decreases by 27% between 580 and 1480 eV. This energy dependence is universally characteristic of poly-crystal and single-crystal materials and is due to a competing increase in true secondary electron generation and a decrease in secondary electron escape with primary electron energy due to secondary electrons being generated deep within the material beyond the escape depth.

Figure 4(a) and the insert of yield at 580 eV show that the total SEE yield decreases as a function of time (the rate itself decreasing with time) before approaching a steady state value that is up to 25% smaller. This follows trends in the AES data which show the decreasing Ni concentration and increasing C and O concentrations [see Fig. 4(b)] and suggests that the change in SEE is due to CO adsorption. CO adsorption on Ni(110) increases the work function⁴⁵–⁴⁷ and, therefore, also increases the energy barrier which secondary electrons must overcome, leading to fewer emitted secondary electrons. Additionally, CO is known to stick strongly to Ni(110) at coverages up to one monolayer for temperatures below 420 K, with the sticking coefficient being initially linear then leveling off. Therefore, the largest change in SEE is expected to occur early when the sticking coefficient is largest, and the surface composition is most rapidly changing, as is observed in Fig. 4(a). The 0 min data in Fig. 4(a) were
determined at each primary energy by linearly extrapolating the first few data points in time.

Note that the concentrations of C and O in Fig. 4(b) are small (e.g., less than 6% during the entire time span investigated). However, concentrations were calculated from AES spectra assuming uniform distributions in the top 10–20 nm of the bulk probed by AES, not by considering that CO lies only on the surface (since a CO molecule is much bigger than a Ni atom). Additionally, peak-to-peak heights were used in the calculation, but the C AES signal may have different line shapes that may change the magnitude of the peak-to-peak height. Therefore, the concentrations in Fig. 4(b) are taken to be qualitative, not quantitative.

Both CO and H₂ are the largest residual gases observed in the chamber by the QMS. Although hydrogen cannot be detected by AES, the authors are confident that there is no H₂ on the surface, since it desorbs from Ni(110) at temperatures below 210 K. Additionally, the decrease in SEE observed in Fig. 4(a) is not due to sample temperature (recall that samples were cleaned and annealed by heating to temperatures up to 1100 K), since a 10% reduction in total SEE yield was observed when the sample was at 327–350 K. Furthermore, recrystallization processes and primary electron dose from the LEED optics were determined to not be the cause of the decrease in Fig. 4(a). Therefore, the high sensitivity of SEE from Ni(110) on adsorbed CO due to the change in the work function was confirmed. Similar sensitivity was observed by Ref. 49 for CO on copper. It should be noted that only a thin layer of CO (<1 monolayer) is adsorbed on Ni(110); therefore, CO adsorption only affects secondary electron escape, not secondary electron generation or diffusion.

Total SEE yields for clean Ni(110) due to primary electrons at 0°, 50°, and 78° (with respect to the sample normal) are presented in Fig. 5. Measurements are compared to previously measured yields from Ref. 21 for primary electrons impacting Ni(110) at 50° and 78°. The agreement between our results and those in Ref. 21 gives confidence in the experimental setup and procedure. Furthermore, our results extend SEE values for Ni(110) beyond 500 eV and show the characteristic peak and decrease in the SEE yield at high incident electron energies due to deeper secondary electron generation. For example, at 0° the yield increases by 39% between 170 and 610 eV, then decreases by 22% between 610 and 1460 eV; this is very similar to the energy-dependent changes observed in Fig. 4(a) at 0 min after cleaning. Also plotted in Fig. 5 is the yield measured by Ref. 15 of SEE from clean polycrystalline Ni; these match other measurements of clean polycrystalline Ni in Refs. 17–19. As can be seen from the figure, SEE from Ni(110) is significantly larger than from polycrystalline Ni (i.e., by up to 36%); the reason for larger SEE from single crystals compared to polycrystalline materials is discussed below. In plasma chemistry applications that utilize Ni(110), such as dry-methane reforming of CO₂ and CH₄, these larger yields may be beneficial since emitted secondary electrons may lead to further fragmentation of CO₂ and CH₄.

The total SEE yields in Fig. 5 increase with an incident angle (i.e., the maximum yield is 1.6, 1.9, and above 2.3 at 0°, 50°, and 78°), as is the general trend for many materials. SEE from polycrystalline materials increases as 1/cos(θ) due to true secondary electron generation being localized in the near-surface region for shallow primary electron penetration (i.e., shallow generation results in secondary electrons undergoing fewer energy-loss collisions en route to the surface and, therefore, maintaining sufficient energies to overcome the surface barrier). Since the primary electron energy at
maximum yield occurs when the primary electron range is equal to the secondary electron escape depth, the primary electron range can be increased for shallow incidence and still remain within the secondary electron escape depth. This shift in primary electron energy at maximum yield towards higher energies has been observed for polycrystalline molybdenum\textsuperscript{50} and is observed in Fig. 5 as well.

However, Fig. 6 shows the SEE for single crystals has a more complex dependence on the primary electron incidence angle. The total SEE yields (normalized by values at $0^\circ$) for 100–990 eV primary electrons incident on as-received Ni(110) as a function of the incident angle are plotted in Fig. 6(a). Data show a maximum at $0^\circ$, minima at approximately $\pm 12^\circ$ and increased yields at larger angles leveling off near $-25^\circ$ and $+35^\circ$. Similar maxima and minima in total SEE yield have been observed for other single crystals,\textsuperscript{22–32,51} including W(110)\textsuperscript{25} whose SEE yield at 2 keV is plotted (in arbitrary units) with data of Ni(110) at 450 eV. Likewise, emission of Auger electrons (also created via ionization collisions by primary electrons) was observed to have similar angular dependencies for gallium atoms on the silicon single crystal.\textsuperscript{52}

The yields are a superposition of the general $1/\cos(\theta)$ curve [plotted in Fig. 6(b)] expected for polycrystalline materials and maxima that correspond to the crystal low-index axes. The maxima are due to an increase in SEE when the primary electrons are directed along the low-index axes, since primary electrons will experience increased scattering with atoms as they penetrate the crystal along close-packed directions. Hence, the positions of the minima/maxima are independent of primary electron energy, as is shown in Fig. 6(a) and are instead dependent on the angle at which the low-index axes make with respect to the sample normal, which is dependent on the crystal structure.

The face-centered cubic (FCC) crystal structure of nickel is plotted in Fig. 7 and the [110] face is highlighted. For the Ni(110) sample, the maximum yield at $0^\circ$ corresponds to the [110] direction and can be seen in Fig. 7(b) to be a closed-packed direction. The [320] direction has an $11.3^\circ$ angle with respect to the [110] direction (for rotation about the [001] axis) and is a low-density direction. Therefore, the minima observed in the SEE yield at approximately $\pm 12^\circ$ is likely due to reduced secondary electron generation along this direction. The large increase over the

FIG. 6. (a) Total SEE yield for 100–990 eV primary electrons impacting as-received Ni(110) at 300 K and $0^\circ–35^\circ$ incidence angles. Lines connecting data points are included, and the data are offset to aid in visualization. (b) Total SEE yield for 450 eV primary electrons. Data from Taub et al.\textsuperscript{55} of 2 keV primary electrons impacting clean W(110) are plotted in arbitrary units for comparison. Additionally, a $1/\cos(\theta)$ curve expected for polycrystalline materials is fit to the Ni(110) data.

FIG. 7. (a) Isometric view of an FCC crystal structure with the [110] face highlighted. (b) Top view of an array of FCC crystal structures. Included are the [110] and [100] low-index directions and other directions of interest.
1/cos(θ) dependence at −20° and +26° may correspond to a relative increase in secondary electron generation along the [210] direction (i.e., 18.4° with respect to the [110] direction). For the W(110) sample (which has a body-centered crystal structure) that is rotated azimuthally, the maximum at 0° corresponds to the [110] direction and the maxima at ±34° correspond to the [111] direction. It should be noted that while the angular positions of the maxima/minima are independent of primary electron energy, the peak amplitude decreases at low primary electron energy such that no maximum is observed at 100 eV. Similar reductions in peak amplitude at low energy were observed by Soshea and Dekker for titanium single crystals and by Palmberg for Ge(111).

The total SEE yields from clean Ni(110) at 300 and 600 K are plotted in Fig. 8 as a function of primary electron energy for primary electrons at normal incidence. The yields are nearly identical (and so also for yields at 50°), which suggests that SEE from clean Ni(110) is independent of temperature within this temperature range. References 53 and 54 found the total SEE yield to be independent of sample temperature for clean polycrystalline metals (i.e., silver and Ni between 725 and 1300 K) since there is a negligible effect on the diffusion of secondary electrons to the surface (i.e., the primary and secondary electron kinetic energies is larger than the sample thermal energy, and there are few secondary electron-phonon interactions). However for single crystals, SEE dependence on temperature may be more complicated. Reference 55 found that the maxima in the angular SEE yield curves for W(110) decrease slightly with temperature due to a reduction in diffraction effects. However, the decrease is less than 5% between 100 and 600 K, hence within our experimental error. Similarly, Ref. 42 found that the work function for clean Ni(110) decreases by only up to 0.07 eV between 300 and 700 K. Therefore, the energy barrier that secondary electrons must overcome in order to be emitted is also relatively unaffected.

Figure 9 shows the total SEE yield measured from Ni(110) at 0° that has been pre-exposed to D2+ (leading to 55% D2 saturation) and measured at 250–265 K. The yield is identical to that of clean Ni(110), since subsurface hydrogen (as opposed to adsorbed surface hydrogen) was likely formed by D2+. Rao also measured a negligible increase in SEE from polycrystalline Ni with subsurface hydrogen, in contrast to the large increase in SEE observed when hydrogen was adsorbed on the surface (i.e., by exposure to a large background of H2 gas at cryogenic temperatures).

IV. CONCLUSION

This effort investigates the dependence of secondary electron emission from a Ni(110) single crystal on primary electron energy and angle, and surface temperature and composition/purity. New measurements of the total secondary electron emission yield showed a complex dependence on the electron incidence angle (i.e., maxima at 0° and minima at ±12°) similar to other single crystal materials, which occurs from enhanced secondary electron generation for primary electrons along closed-packed crystalline directions. This result in secondary electron emission from clean Ni(110) that is 36% larger at 0° (i.e., primary electrons along the [110] direction) as compared to clean polycrystalline nickel. The yield was found to be highly dependent on incident electron energy between 0 and 500 eV and to decrease by up to 25% due to adsorption of carbon monoxide from the chamber background. In contrast, yields were found to be independent of sample temperature between 300 and 600 K and identical for clean and D2+-exposed Ni(110) at the exposures considered herein (i.e., 2 x 10⁻⁸ Torr for 150 s).

The results illustrate the significant difference in secondary electron emission from the single crystal versus polycrystalline materials and the need to accurately consider crystal orientation (i.e., to calculate a priori the incident angles corresponding to closed-packed directions). In addition, results are important for plasma-enhanced chemistry that utilize Ni(110) catalysts, such as plasma-enhanced dry reforming of methane (i.e., CO2 + CH4 → 2H2 + 2CO). For example, the larger secondary electron emission of a Ni(110) single crystal will lead to more low energy secondary electrons that may facilitate further reactions of surface-adsorbed species. However, the opposite is likely to occur for surfaces with adsorbed carbon monoxide.

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