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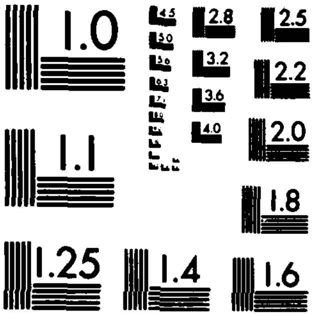

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A STUDY OF THE SPUTTERING PROCESS
BY ION-INDUCED OPTICAL EMISSION

Final Progress Report
for Period January 1, 1981 - August 31, 1981

I. S. T. Tsong

Prepared for the Office of Naval Research
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REPORT

In the final eight-month period of this project from January 1 to August 31, 1981, we have carried out the following experiments:

(1) Bombardment of a clean single crystalline Ni target by Ne^+ ions at 15° incident angle from the (110) surface. The yield of the scattered Ne^+ ions, detected at an angle of 30° from the primary beam direction, was measured as a function of the azimuthal angle by rotating the Ni target along its <110> axis. The excited NiI and NeI emissions were also detected as a function of the azimuthal angle. Correlation among the scattered Ne^+, excited NiI and NeI yields points to a mechanism whereby the final collision in scattering and sputtering gives rise to excitation. Full details of this experiment are given in Appendix I.

(2) Similar experiment as in (1), but with oxygen coverage on the surface. The results from this experiment are only preliminary. Further work is required to understand the role of oxygen in the excitation process. Both experiments (1) and (2) were carried out in Bell Laboratories in collaboration with Dr. N. H. Tolk.

(3) Bombardment of Si and Ge with N_2^+ ions to examine the molecular spectra of N_2 and N_2^+. Snowdon, Heiland and Taglauer in Germany have recently proposed a novel mechanism in which processes involving two-body associative ionization and diabatic curve-crossing appear to account for the observed molecular spectrum. In our experiment, we performed simultaneous photon and secondary ion detection to confirm the existence of N_2^+ after collision. We also studied the molecular emission with much higher resolution than Snowdon et al. A full discussion of our results will appear later after we have performed detailed data analysis.

(4) Bombardment of a series of Cu/Ni alloys to study the effect of matrix composition on the photon and secondary ion yields. The experiment was performed on clean surfaces as well as a function of oxygen coverage. Previous work by Loxton et al. in Australia has shown anomalous enhancement effects by oxygen on the photon yields of each individual component of Nb/V alloys. We selected Cu/Ni alloys for our study because the oxidation and preferential sputtering effects in these alloys are well-known.

Throughout the 38-month period of this project, we have produced 1 Ph.D. thesis, 1 M.S. thesis, 11 publications and presented 6 papers in conferences. We hope to continue in a similar vein at Arizona State University.

PERSONNEL

Christopher M. Loxton of the Australia National University started his postdoctoral position on this project on June 1, 1981. Nihad A. Yusuf successfully defended his Ph.D. thesis in May 1981.

THESES COMPLETED

Ph.D. Thesis: Nihad A. Yusuf. "Outershell Excitation in Sputtered Atoms". The Pennsylvania State University (May 1981)

M.S. Thesis: Seiji Tsuji. "The Enhancement of Photon Yield from Ion-Bombarded Surfaces by Adsorbed Oxygen". The Pennsylvania State University (May 1980)

PAPERS IN PRESS

I.S.T. Tsong, N.H. Tolk, T.M. Buck, J.S. Kraus, T.R. Pian and R. Kelly. Outershell Electronic Processes in Ne^+ Collisions With a Ni(110) Surface. Nucl. Instrum. Meth.

S. Tsuji, I.S.T. Tsong and S.V. Krishnaswamy. The Influence of Oxygen on the Continuum Emission from Ion-Bombarded Metal Surfaces. Spectrochim. Acta.

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I.S.T. Tsong and N.A. Yusuf. "Velocity Measurements of Sputtered Atoms in Excited States." Nucl. Instrum. Meth. 170 357-362 (1980).

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P. Williams, I.S.T. Tsong and S. Tsuji. "A Comparison of Absolute Yields of Excited Neutrals and Positive Ions from Ion-Bombarded Surfaces." Nucl. Instrum. Meth. 170 591-595 (1980).

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N.A. Yusuf and I.S.T. Tsong. Kinetic Energies of Excited Atoms Ejected From Ion-Bombarded Surfaces. Surface Sci. 108 578-586 (1981).

PAPERS PRESENTED IN MEETINGS

"Edge-Effects Correction in Depth-Profiles Obtained by Ion-Beam Sputtering"
4th International Conference on Ion Beam Analysis, Aarhus, Denmark (June 1979)

"Velocity Measurements of Sputtered Atoms in Excited States"
8th International Conference on Atomic Collisions in Solids, Hamilton, Canada (August 1979)

"A Comparison of Absolute Yields of Excited Neutrals and Positive Ions From Bombarded Surfaces"
8th International Conference on Atomic Collisions in Solids, Hamilton, Canada (August 1979)

"A Comparison of Absolute Yields of Excited Neutrals and Positive Ions From Ion-Bombarded Surfaces"
2nd International Conference on Secondary Ion Mass Spectrometry, San Francisco (August 1979)

"Quantitative Aspects of Outer-Shell Excitation in Ion-Surface Collisions"
3rd International Workshop on Inelastic Ion-Surface Collisions, Feldkirchen-Westerham, Fed. Rep. Germany (September 1980)

"Outershell Electronic Process in Ne^+ Collisions With a Ni(110) Surface"
9th International Conference on Atomic Collisions in Solids, Lyon, France (July 1981)

APPENDIX 1

OUTERSHELL ELECTRONIC PROCESSES IN Ne^+ COLLISIONS WITH A Ni(110) SURFACE

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T. J. Watson Research Center, IBM Corp.
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ABSTRACT

By performing simultaneous detection of forward-scattered $Ne^{\pm}$ ions and photons emitted by Ne and Ni excited atoms when a Ni(110) surface was bombarded by 4 keV $Ne^{\pm}$ ions at near-grazing incidence, we studied the ion and photon yields as a function of the azimuthal angle. The variations observed in the yield anisotropies show the different degrees of influence of the surface structure on outershell electronic processes during ion-surface collisions.

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1. INTRODUCTION

The phenomenon of outer-shell excitation during ion-surface collisions leading to ejection of particles which radiate above the surface is well-known, and numerous studies have been conducted in the past decade.[1] Intensive efforts notwithstanding, many details required to shed light on the precise mechanism responsible for excitation are still lacking. Here we present correlated experimental data on excitation that occurs via two distinct collisional processes: one involving collisions resembling binary encounters between incoming primary ions and surface atoms and the other involving collisions occurring at depths which are atomically large inside the solid.

Previous work has demonstrated that when a single crystalline target is bombarded by energetic (>50 keV) heavy ions, anisotropy in the photon yields of sputtered excited atoms can be observed depending on whether the primary ion beam is aligned with transparent or opaque crystallographic directions.[2,3] Work on low energy ion scattering has also shown that surface anisotropy of a single crystal can influence the reflection of low energy (<5 keV) noble gas ions from the target surface.[4-7] In the present work we carried out simultaneous detection of scattered ions from a single crystal Ni(110) surface as well as photons emitted by sputtered and scattered particles. By comparing the anisotropies in the two types of photon yield (i.e., from sputtered and scattered particles) with the anisotropy of scattered ion yield as a function of azimuthal rotation, we observe that the two collisional processes involve similar if not identical excitation mechanisms. These are the first simultaneous, correlated measurements of these outershell effects.

2. EXPERIMENTAL AND RESULTS

The experimental arrangement is depicted in Fig.1. The 4 keV mass-analyzed Ne^+ ion beam made an incident angle $\psi = 15^o$ with the Ni(110) target surface. The scattering angle, θ, was 30^o and the energy of the forward-scattered Ne^+ ions was measured with a 127^o electrostatic analyzer. The target sample was rotated azimuthally through its <110> axis in 2^o steps. The total variation in azimuthal angle, ϕ, was limited to 130^o. The photons were collected by a quartz lens and directed into a 0.3 m McPherson monochromator with its optical axis perpendicular to the beam direction. The base pressure of the target chamber was 1×10^{-9} torr. The Ne^+ beam current density was 0.1 $\mu A\ mm^{-2}$.

Ne^+ was chosen as the bombarding ion in order to perform both scattering and sputtering functions. To observe scattering from impurity species such as oxygen which is lighter than Ne, we performed the scattering in a forward direction. The small-angle, 30^o, forward-scattering configuration also enhances the anisotropy effects due to shielding of atoms in the second layer by the first layer on the Ni(110) surface (Fig. 2). Fig. 3 shows the energy spectra of forward-scattered Ne^+ before and after cleaning of the Ni target surface. The O and S peaks (in curve a) disappeared leaving only the Ni peak after repeated heating and bombardment cycles (curve b).

Figure 4 shows the variations as a function of azimuthal rotation of the Ni crystal of (a) the scattered ion yield of Ne^+ from Ni, (b) the photon yield of scattered Ne radiation at 6402 Å and (c) the photon yield of the sputtered Ni at 3524 Å. The scattered Ne^+ yield was measured by integrating the area under the Ni peak in the energy spectrum (Fig. 2b). The photon yields were measured simply by counting the number of photons per second at the peak height of each of the two appropriate spectral lines.

3. DISCUSSION

The crystallographic directions marked on the azimuthal angle of rotation ϕ, i.e., the x axis in Fig. 4, correspond to those azimuthal directions with which the incident beam was aligned. For the NiI 3524 Å yield in Fig. 4(c), pronounced minima can be observed when the primary beam is aligned with the $[1\bar{1}0]$, $[1\bar{1}2]$ and [001] azimuths of the target crystal. This is not too surprising, considering the fact that these directions correspond to the planar channels in the crystal (see Fig. 2). Since the normal component of the primary beam energy is about 1 keV, the observed dips in the NiI excited yield are equivalent to the familiar drop in sputtering yield when an ion beam aligns with the main planar channels in a single crystalline target. Such azimuthal dependence has also been observed in low energy SIMS work.[8]

This channeling effect implies that the collisions leading to the sputtering of excited Ni atoms occur from a depth in the solid appreciably greater than one atomic layer. However, this is not equivalent to saying that the excited atom was formed at some depth inside the solid and emerged as such since the mean diameter of an excited atom is considerably greater than the interatomic spacing making it inconceivable that such an atom can move about in a solid. Rather, the channeling dips in the azimuthal dependence of the NiI 3524 Å emission suggests that the sequence of collisions giving rise to a sputtered atom occurs in part within the solid and depends on the depth in which the energy is deposited. As the chain of recoil atoms finds its way to the surface, the final collision with the topmost atom results in sputtering of that atom.[9,10] It is clear that excitation results from the final interaction with a surface atom with the subsequent photon emission taking place after the atom has left the surface. Such excitation may result from a level-crossing mechanism[11-14] similar to that proposed by Fano and Lichten[15] for atomic collisions in the gas phase.

The NeI 6402 Å emission (Fig. 4b) however, displays a somewhat different behavior. The azimuthal dependence shows minima at $[1\bar{1}0]$ and $[1\bar{1}2]$, but a maximum at [001]. The anisotropy exhibited is entirely analogous to that of Ne^+ scattered from Ni (Fig. 4a). Since it is well-known that in low energy ion scattering spectrometry, scattering events which occur below the surface layer result in a high probability of neutralization of the projectile ion, we can safely assume that in our energy regime (4 keV Ne^+ at 15^o incidence angle with the surface) the anisotropy observed in the azimuthal dependence of the scattered Ne^+ is entirely due to the first and second layers of the Ni atoms on the (110) surface. The similarity between the NeI 6402 Å and the scattered Ne^+ anisotropies therefore implies that the excited Ne atoms were formed from collisions resembling binary encounters between the incoming Ne^+ ion and the surface Ni atoms, resulting in scattered Ne excited atoms which decay above the surface and give rise to the NeI 6402 Å emission. If the excitation of the Ne atoms is the result of neutralization events occurring deeper inside the solid, then one would expect that the anisotropy in the azimuthal dependence to be similar to that of NiI 3524 Å (Fig. 4c). This was in fact observed when we bombarded a Ni(100) surface with 9 keV Ne^+ ions at incident angle $\psi = 55^o$, the anisotropy in the azimuthal dependence of the photon yields of NeI 6402 Å and NiI 3524 Å lines were identical.[16]

From the different behavior in the azimuthal dependence of the sputtered NiI (Fig. 4c) and the scattered Ne$^+$ and NeI (Fig. 4a and b), it is clear that the planar channeling effects observed in the case of NiI do not operate in the same way in the scattered Ne$^+$ and NeI emission. It is possible that in our small-angle forward-scattering configuration, the observed anisotropies in Figs. 4a and 4b are due to neutralization effects in the ion-surface scattering process. Let us consider Ne$^+$ in Fig. 4a where scattering occurs from both the first and second layer, i.e., along the $[1\bar{1}0]$ and $[001]$ azimuths in Fig. 2. Due to the closer spacing of atoms along the $[1\bar{1}0]$ azimuth, a Ne$^+$ ion aligned with $[1\bar{1}0]$ has, on both its inward and outward trajectories at 15° to the surface, a much greater probability of being neutralized by interacting with the nearest neighbor atom from the scattering center. Conversely, the wider spacing of atoms along the $[001]$ azimuth, which insures less neutralization, gives rise to the maximum in the azimuthal dependence of scattered Ne$^+$ (Fig. 4a).

When the ion beam is aligned with $[1\bar{1}2]$, i.e., $\phi = 54.7^\circ$ in Fig. 2, scattering only comes from the first layer because atoms in the second layer are shielded by the first. Although there is less neutralization because the spacing of the first layer atom is wide apart, the total number of scattering events is however reduced due to the shielding. Therefore a minimum is observed at the $[1\bar{1}2]$ azimuth (Fig. 4a). The same argument can be applied to explain the maximum at $\phi = 67^\circ$ in Fig. 4. Referring again to Fig. 2, it can be seen that when the beam is aligned with $\phi = 67^\circ$, the first layer atoms are very wide apart causing less neutralization and some scattering can arise from the second layer because they are now only partially shielded. Therefore we observe a maximum at this azimuth in Fig. 4a ($\phi = 67^\circ$ from the $[1\bar{1}0]$ azimuth).

The similarity between Figs. 4a and 4b implies that neutralization by nearest neighbor atoms results in ground state neutrals rather than excited states. If excited states were produced, then one would expect the azimuthal dependence of Ne 6402 Å line to exhibit an opposite trend to that of scattered Ne^+ ions. This similarity suggests the possibility that the excited state of NeI is formed during the collision of the scattering event. However, there is also the possibility of excitation as a result of the scattered Ne^+ picking up an electron into an excited orbit when it is some distance, say 5 Å, from the surface. The second possibility can also account for the similarity between the Ne^+ and NeI anisotropies since the crystallinity of the surface will not have an influence when the Ne^+ is a long way from the surface when the electron pick-up takes place.

We have also carried out preliminary calculations using the ARGUS computer code[17] supplied by D.P. Jackson for the scattering of neon from a (110) Ni surface. The calculations reproduce some of the major features observed in the scattered Ne^+ and the NeI emission, i.e., the minimum at $[1\bar{1}0]$ and the maximum at [001]. However, other features do not reproduce. This is likely due to the fact that different collision trajectories (either involving different layers or multiple collisions and focussing) contribute to neutralization and excitation with different probabilities. Further calculations are now under way to take these factors into account.

4. CONCLUSION

We have identified two distinct processes leading to outershell excitation, one from scattered particles after having undergone bi-particle collisions with surface atoms and the other from sputtered particles which are initiated by a multiple collision chain originated from atomically large depths. Our data suggest that they both share a common excitation mechanism, namely, the final collision which gives rise to scattering or sputtering. Such a mechanism bears strong similarity to that occurring in gas phase collisions via curve-crossing processes.[15]

ACKNOWLEDGEMENT

One of us (ISTT) wishes to acknowledge support from the Office of Naval Research (L.R. Cooper) and from Bell Laboratories.

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FIGURE CAPTIONS

Fig. 1 Schematic diagram of experimental set-up for simultaneous detection of low energy ion scattering and photon emission.

Fig. 2 Model of the Ni(110) surface showing the first and second layer atoms.

Fig. 3 Energy spectra of Ne$^+$ scattered from (a) a contaminated and (b) a cleaned Ni(110) surface.

Fig. 4 Azimuthal dependence of (a) scattering yield of Ne$^+$ from Ni (b) photon yield of NeI 6402 Å and (c) photon yield of NiI 3524 Å. ϕ is the angle of rotation of the Ni crystal. These yields are normalized to the maximum yield in each case and the curves are displaced for clarity.

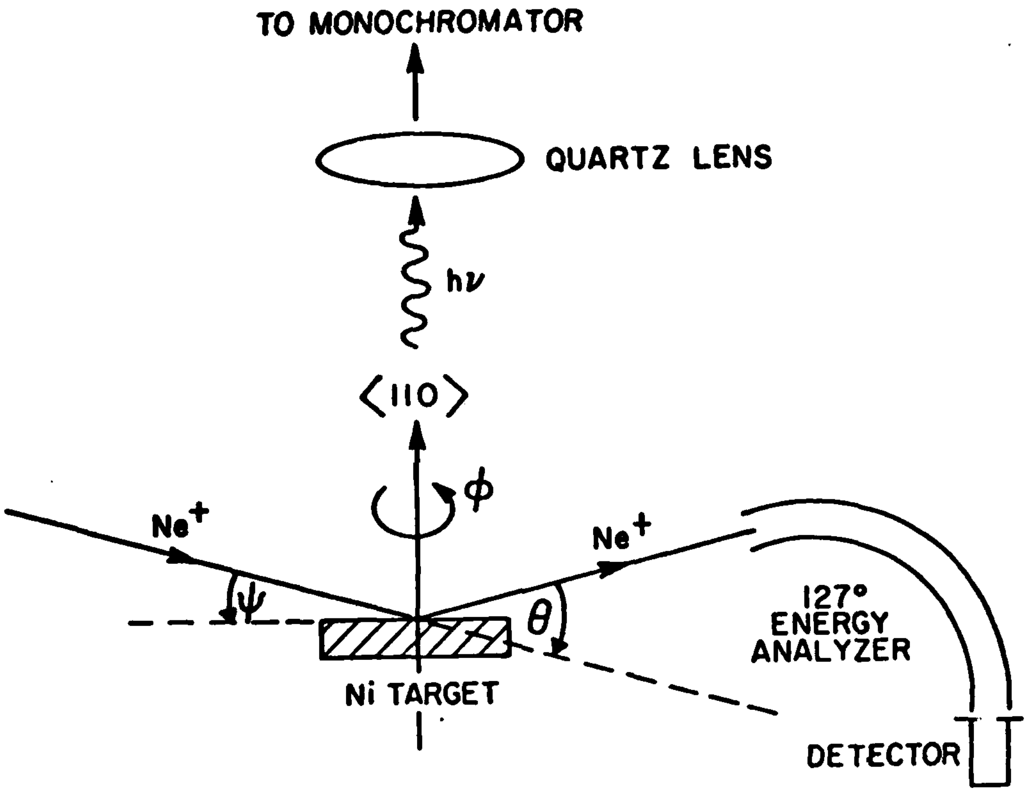
TO MONOCHROMATOR
QUARTZ LENS
hν
⟨110⟩
φ
Ne+
ψ
Ne+
θ
Ni TARGET
127°
ENERGY
ANALYZER
DETECTOR

FIG. 1

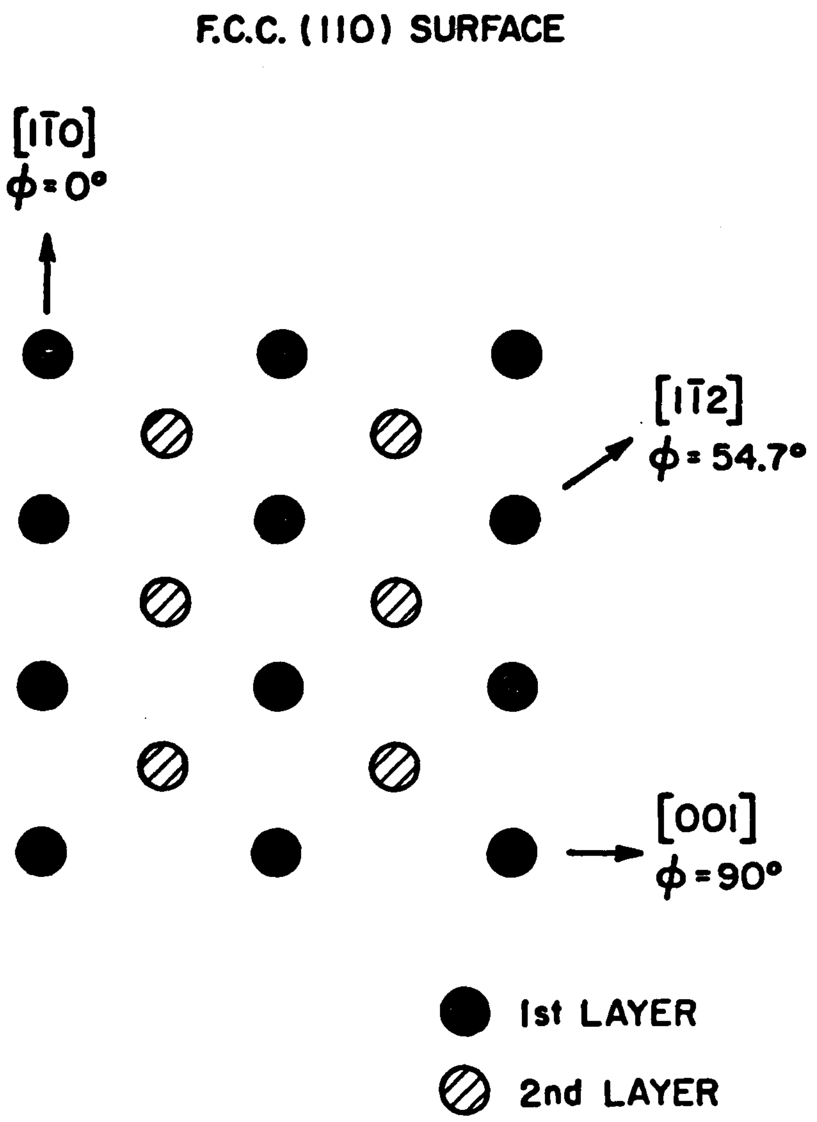
F.C.C. (110) SURFACE
$[1\bar{1}0]$
$\phi = 0°$
$[1\bar{1}2]$
$\phi = 54.7°$
$[001]$
$\phi = 90°$
● 1st LAYER
▨ 2nd LAYER

FIG. 2

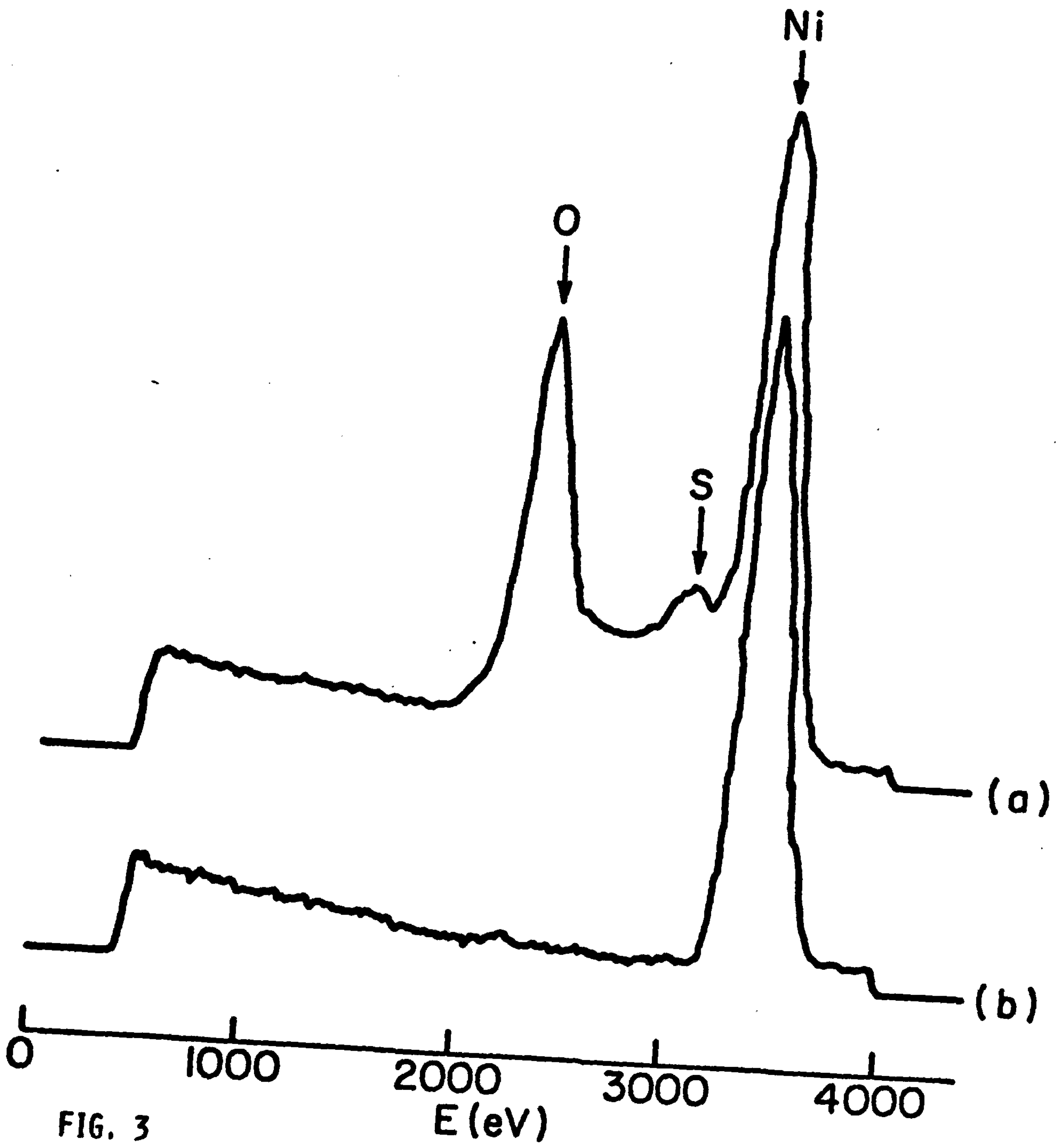

FIG. 3

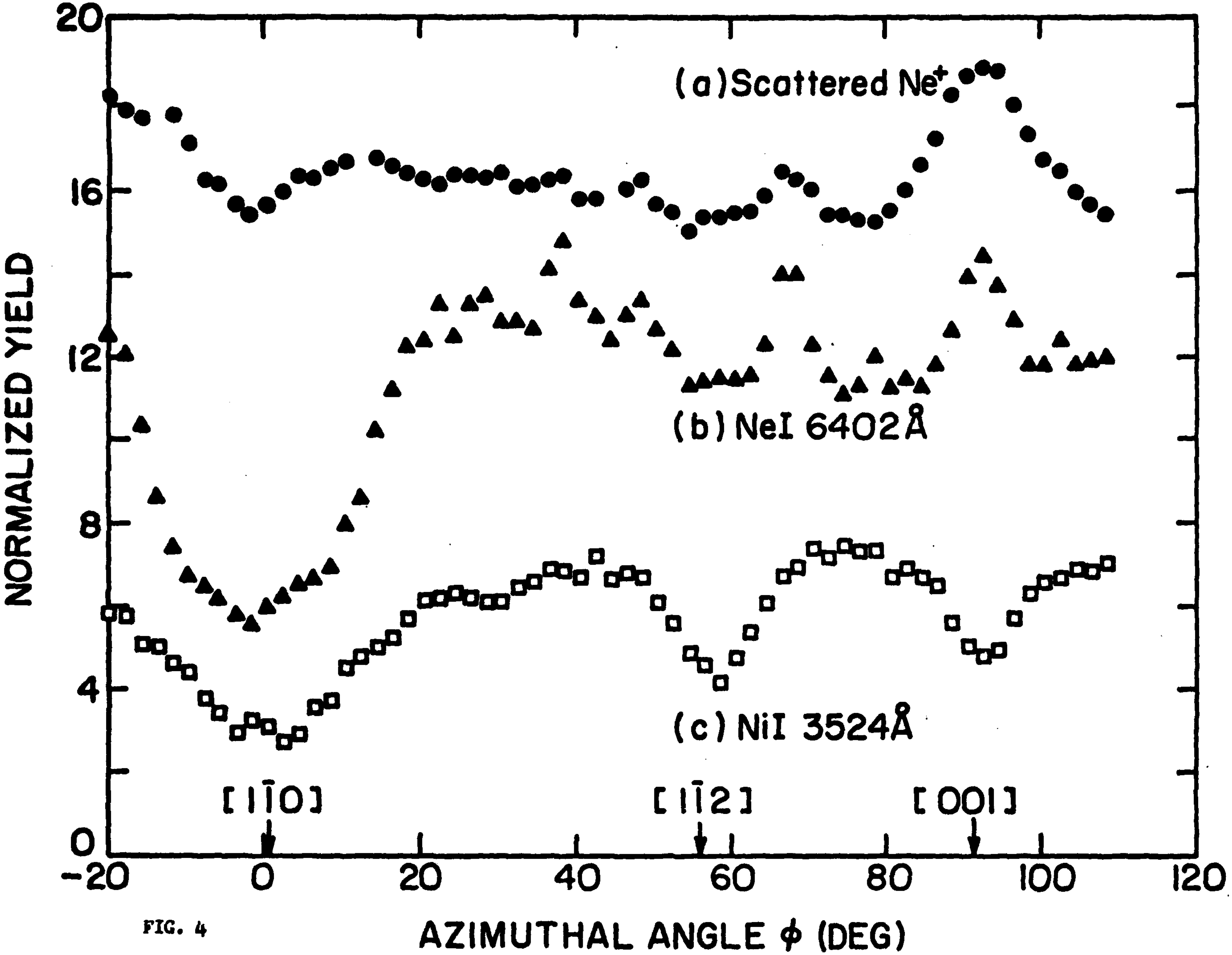
(a) Scattered Ne^+
(b) NeI 6402Å
(c) NiI 3524Å
[1$\bar{1}$0]
[1$\bar{1}$2]
[001]
NORMALIZED YIELD
0
4
8
12
16
20
-20
0
20
40
60
80
100
120
AZIMUTHAL ANGLE ϕ (DEG)

FIG. 4

DAT

FILM