Velocity distribution and yield measurements of Fe ejected from FeS₂ during ion bombardment

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Secondary neutrals sputtered by 3-keV Ar⁺ from FeS₂ and Fe were studied by use of laser postionization mass spectrometry and laser-induced fluorescence spectroscopy. The velocity distribution and yield of Fe from the FeS₂ sample were measured. The velocity distribution of Fe sputtered from the sulfide is very similar to that of sputtered Fe from the pure metal with both distributions peaking at nearly the same velocity. The yield of Fe from the sulfide target, after prolonged bombardment, was at most 27% of the yield from the metal. The results are compared with Monte Carlo calculations using the TRIM (transport of ions in matter) code. The total sputtering yield of FeS₂ was measured using profilometry and was compared with the same measurements of the sputtered metal targets. The surface of the FeS₂ was examined by x-ray photoelectron spectroscopy before and after ion bombardment and indicates preferential sputtering of S at low primary ion doses. After prolonged bombardment, the surface becomes similar to that of FeS. The profilometry measurements and the yield measured by mass spectrometry indicate that some of the sputtered Fe is not observed in the neutral ground state; we propose that the unobserved Fe is in the form of clusters.

I. INTRODUCTION

Ion-beam sputtering of compounds is an important and complex problem. Some of the complexities stem merely from the presence of a second component in the target, while others are results of chemical interactions between the species. Since compound materials have many technological applications (e.g., III-V and II-VI semiconductors, high- T_c superconductors), it is important that we be able to understand and use sputter-based techniques on them. Some issues associated with multicomponent targets, such as preferential sputtering and surface segregation, have been the subject of previous investigations in alloys and isotopes.¹⁻⁶ However, the sputtering phenomenon cannot be viewed in terms of collisional aspects alone because the chemical nature of the materials is a factor in the mechanism for removal of species from the solid. This makes interpretation of results quite complicated. Unfortunately, due to these apparent complexities, theoretical treatments are at the early stages^{7,8} and the few experimental studies (mainly on alkaline halides^{9,10} and oxides^{11,12} and few other compounds¹³) do not give a clear picture of the phenomenon.

To understand the mechanism of sputtering in compound targets, the partial yield of the individual constituents, including the molecules and clusters formed by them, as well as the angular distribution of the sputtered species should be known. This is a significant factor when, for example, ion-beam sputtering is used for thin-film deposition of CuO or Y₂O₃ for a high- T_c supercon-

ducting material.¹⁴ Changes in the stoichiometry, the flux as a function of the ejection angle, and the sputtering rate due to the dynamics of sputtering are all important issues and need to be addressed. A technique applicable to the study of compound material sputtering is SIMS (secondary ion mass spectrometry) analysis. Typically, the probe beam used in SIMS is oxygen. After prolonged sputtering of the material, the embedded oxygen can form an oxide in the target. The rate and distribution of sputtered species will be affected by the formation of the oxide, which in turn will affect the results of the analysis.¹⁵

While unable to address all of the above issues, we have studied some of the effects of ion-beam bombardment of a compound. We have chosen FeS₂ for this study because it contains Fe, which has previously been studied extensively in pure metallic form¹² and in different matrices (such as Mo and Si,¹⁶ steel and Ni₃Fe,¹⁷ and stainless steel¹⁸). In order to understand the nature of the sputtering regime for FeS₂ under 3-keV Ar⁺ bombardment, we have measured the velocity distribution of sputtered Fe from the FeS₂ target in the high primary ion dose after the surface has become amorphized. This was accomplished by the method of Doppler-shift laser-induced fluorescence spectroscopy (LFS). The total sputtering yield of FeS₂ was measured by profilometry to make quantitative comparisons with real time partial yield measurements of Fe. The Fe partial yield measurements were conducted as a function of the primary ion dose and were quantified by comparison with results from a pure

Fe target. These measurements were performed both on the SARISA (surface analysis by resonance ionization of sputtered atoms) apparatus and the LFS apparatus at Argonne National Laboratory.

X-ray photoelectron spectroscopy (XPS) studies were performed to examine surface composition for low and high dose ion bombardment in the vacuum generators (VG) surface probe instrument at Caltech. In addition, the experimental measurements were compared with TRIM (transport of ions in matter¹⁹) Monte Carlo calculations of the sputtering yields. The TRIM code was used to estimate the yield and angular distribution of the sputtered species, since species sputtered from a multicomponent target may have a different angular distribution than the same species sputtered from an elemental target. This becomes a concern when signals from the two targets are compared at a given angle for characterization of the multicomponent material. The detection angle of SARISA was examined in relation to this concern.

II. VELOCITY DISTRIBUTION

The velocity distribution of sputtered species contains valuable information about ion-surface interactions. Besides being indicative of the sputtering mechanism, it also can help estimate the yield of the sputtered species.¹⁵ According to the sputtering theory for elemental metal targets in the collisional cascade regime, the sputtering yield and the surface binding energy are inversely proportional. In addition, the peak of the energy distribution is dependent on the surface binding energy of the atom to the target.

The velocity distribution of ground-state Fe sputtered from Fe and FeS₂ targets were measured by Doppler-shift laser-induced fluorescence spectroscopy in an ultrahigh vacuum (UHV) chamber designed specifically for this purpose. The LFS method employed and the instrument used are described in general terms elsewhere.²⁰ Specific details for these measurements are described below. The FeS₂ sample was cut from a natural single crystal with a diamond saw, cleaned ultrasonically with trichloroethylene, acetone, and methanol, and placed in the UHV chamber. Although the sample was a single crystal in the initial stages of all the experiments, the measurements of the yield and velocity distribution were taken after the sample had received a high primary ion dose. It has been shown that for high ion dose the sample is amorphous to a depth that is beyond where the particles are ejected during ion bombardment.^{21–23} Therefore, we are not concerned with the original crystalline nature of the target.

Figure 1 shows a partial energy diagram for Fe including its ground multiplet states. The transition used was from a^5D_4 to y^5D_4 , requiring 302-nm excitation photons. The dye used in the ring dye laser (Spectra Physics 380A pumped by a Spectra Physics 171 Ar-ion laser) is Rhodamine 6G, while the amplifier cells, pumped by a XeCl excimer laser (Lumonics TE181T), contained Rhodamine B. The first amplifying cell contained a small amount of Kition Red as well.

The details of the data conversion and interpretation

can be found in Refs. 20 and 24. As has been shown by Young *et al.*²⁰ and Wright *et al.*,²⁴ the LFS signal is proportional to the number density of the atoms in the detection volume. The atomic absorption that produces the fluorescence is Dopplershifted because of the motion of the sputtered atoms relative to the direction of laser propagation. During each run, the laser is scanned in a 30-GHz interval and the fluorescence signal is obtained as a function of the frequency. Using the Doppler broadening relation

$$\nu \propto \nu_0(1 + v \cos \theta / c), \quad (1)$$

where ν is the observed frequency, ν_0 is the zero-velocity frequency of transition, θ is the angle between the laser and the direction of the traveling atom, v is the velocity of the atom, and c is the speed of light, the LFS signal versus frequency is converted to the number density distribution $N(v)$ in the component along the laser beam, approximately normal to the surface.

The measured velocity distribution of Fe sputtered from a FeS₂ target is plotted in Fig. 2. Each data point in Fig. 2 is an average of 50 laser shots and the signal is the running average of the data. The dashed line is the

FIG. 1. A partial energy diagram of the Fe atom. The arrows on the right show the transitions that were used for the excitation and the fluorescence in the LFS experiments and the arrows on the left show the three-color ionization scheme used for the RIMS experiments.

Sigmund-Thompson^{25,26} velocity distribution, which has the form

$$N(v) \propto v^2 / (v^2 + v_b^2)^3, \quad (2)$$

where v_b is a characteristic velocity that corresponds to the binding energy E_b of atoms to the surface of the target as $E_b = mv_b^2/2$. From Eq. (2) it can be shown that the distribution peaks at $v_b/\sqrt{2}$. For an elemental target, the surface binding energy is usually estimated from the heat of sublimation of the material. In the Sigmund-Thompson distribution shown in Fig. 2, v_b corresponds to the binding energy of a pure Fe target ($E_b = 4.315$ eV).²⁷ As seen in Fig. 2, there is very good agreement between the Sigmund-Thompson distribution and the data. The separation of the experimental and theoretical peaks corresponds to a binding energy difference of ~ 0.2 eV between Fe sputtered from Fe and FeS₂.

The above result reveals two significant facts about the sputtering of FeS₂. First, the sputtering of FeS₂ is in the collisional cascade regime and second, the binding energy of Fe is very similar for Fe and FeS₂, predicting a stoichiometric partial yield of Fe from FeS₂. In other words, the sputtering yield of Fe (summed over all possible Fe channels) from FeS₂ should equal 1/3 the yield of Fe sputtered from a pure Fe target.

III. YIELD MEASUREMENTS

In a binary compound, the composition of the sputtering yield is somewhat more complicated than in elemental sputtering. For a metal sulfide, the sputtering yield can be described as the partial sputtering yields of the metal atom, sulfur atom, and molecules (e.g., FeS and S₂),

FIG. 2. Velocity distribution of sputtered Fe from an FeS₂ target. The dashed line is a Sigmund-Thompson distribution, normalized to the signal amplitude, with the peak velocity calculated from the binding energy of Fe from an Fe target.

respectively. Each partial sputtering term is summed over the different electronic and ionic states of the species. In the case of molecules, the sum is also over the various vibrational and rotational states of each molecular species. Due to the differences in mass and binding energy of each constituent, preferential sputtering of one of the components of the target might well occur, thus changing the stoichiometry of the near surface region of the sample. Steady-state conditions (where the rate of ejection of the two constituents is equal to their stoichiometry) should be reached after prolonged bombardment of the sample. We have estimated the partial yield of Fe from FeS₂ as a function of the primary ion dose, using LFS and RIMS (resonance ionization mass spectrometry) for detection of ground-state Fe atoms, and NRIMS (nonresonance ionization mass spectrometry) for detection of Fe atoms summed over its various states. In order to quantify the partial sputtering yield of Fe, we obtained the total sputtering yield of FeS₂ by profilometry in which total yield was defined as the yield of FeS₂ molecule per Ar⁺ ion. Assuming that all Fe is sputtered as atoms then the partial yield of Fe from FeS₂ is the same as the total yield of FeS₂ as defined above. The measurement techniques will be described in the following sections.

A. LFS yield measurements

The samples used for these measurements were pure Fe and natural FeS₂. The LFS intensity of atomic Fe from both the pure elemental and FeS₂ targets were measured under the same geometric configuration. The signals were then compared taking into account the laser intensity and the primary ion current. Since the fluorescence signal intensity is proportional to the product of the square root of the probe laser intensity²⁸ (an approximate result of power broadening in the case where laser bandwidth is much less than Doppler frequency width) and the primary ion current, the two LFS signals can be scaled for direct comparison. Furthermore, since the LFS signal is proportional to the number density of sputtered atoms as described in Sec. II, the ratio of the two signals after the above normalization is a measure of the difference in the sputter yield from the two targets. We have observed that the Fe signal from FeS₂ is about 18% of the signal from the pure Fe target after the FeS₂ target has been bombarded to a fluence of $\sim 0.5 \times 10^{17}$ ions/cm².

B. RIMS yield measurements

While RIMS measurements are state specific, as are the LFS measurements, RIMS performed in the SARISA apparatus has a higher detection solid angle when compared to the LFS setup. A detailed description of the SARISA apparatus and the technique can be found in Refs. 29 and 30. Briefly, a 3-keV Ar⁺ strikes the surface at normal incidence. Some of the secondary neutrals generated by the ion beam are ionized by the laser and detected in a time-of-flight mass spectrometer. Figure 3 is a schematic drawing of the experiment, concentrating

on the detection volume and the acceptance angle of the SARISA apparatus. The laser is typically about 1 mm away from the target. The 3-mm detection length in the direction parallel to the laser beam is due to the ion-beam extraction optics solid angle. This geometry provides a $\pm 60^\circ$ acceptance angle,²⁹ which is shown schematically in Fig. 3. Considering the large angle of acceptance of the SARISA apparatus, the majority of the sputtered species is detected in the mass spectrometer once ionized.

The polycrystalline Fe and the single-crystal FeS₂ were sputtered in the SARISA apparatus, and RIMS was used for the interrogation of the sputtered Fe. An energy diagram of Fe showing the resonance ionization scheme that was used is given in Fig. 1.

The RIMS measurements were three-color experiments employing three tunable dye lasers. The output from a single Questek model 2660 XeCl excimer laser was split in order to pump all three dye lasers. Two Lumonics dye lasers (one employing Coumarin dye lasing at 510 nm and the other PTP dye lasing at 344 nm) and a Moletron laser (employing DCM dye lasing at 640 nm) were utilized in these experiments. Saturation of each transition was studied as a function of the laser power. The first two resonant steps were found to be saturated, while the third (ionization) transition was not.

RIMS measurements on the pure Fe target were performed first, after sputter cleaning its surface. An FeS₂ sample was then moved into the beam line and was examined by RIMS. Because of possible preferential sputter-

ing, the ion dose to the FeS₂ was carefully recorded during sputter cleaning. Three data points were taken as follows: a RIMS measurement was taken on the virgin sample, next the sample was raster sputtered for 1 min followed by a RIMS measurement, then rastered for a 2-min interval followed by a RIMS measurement. During the sputter cleaning the ion current was 3 μ A and the raster area was 1 mm $\times$ 1 mm. The Fe sample was then brought back to the beam line, and the RIMS measurement on the Fe sample was repeated to check reproducibility. The results of these measurements are plotted in Fig. 4. The ratio of the Fe signal from FeS₂ to that obtained from pure Fe is 0.19 in the high ion dose limit. This agrees with the LFS results but is lower than expected from stoichiometric considerations.

C. NRIMS yield measurements

Sputtering yields from Fe and FeS₂ were also examined by NRIMS measurements in the SARISA apparatus. This method was used for monitoring simultaneously the signal level of different sputtered species and for accessing atoms in excited states.

The partial yield of Fe sputtered from FeS₂ was measured as a function of primary ion dose in order to gain insight into sputtering dynamics. The primary ion dose was administered by rastering the ion beam for different time intervals followed by NRIMS measurements. Throughout these rastering and measurement cycles care was taken to insure that changes in the transmission of the machine did not occur. As with the RIMS measurements, to separate such apparatus effects from the sputtering mechanism, a reference point was chosen on the sample that was not dosed. Data were collected from

FIG. 3. A schematic of the experimental layout in the SARISA apparatus. The detection angle is determined by the distance of the laser from the target and the transmission characteristics of the ion optics (Ref. 29).

FIG. 4. The ratio of partial yield Fe from FeS₂ and from Fe as a function of the primary ion dose. The RIMS data were obtained by a three-color experiment and the NRIMS experiments employed a KrF excimer laser. The first two or three points of the NRIMS data are indicative of cleaning the target. The change in the ratio demonstrated here is due to the changes in the Fe signal from the FeS₂ target, since no change in the Fe signal intensity from the Fe sample was observed as a function of ion dose.

the reference point periodically to confirm that no changes occurred from measurement to measurement.

In a typical experimental run, measurements were performed first on a sputter-cleaned Fe target. The FeS₂ sample was then situated in the beam line for analysis. The FeS₂ sample was moved up 1 mm from its center position and measurements were conducted as a reference. The sample was moved down from the center by 1 mm and mass spectra were taken as a function of ion dose. Additional measurements on the reference point were performed after every two or three raster and measurement cycles. Figure 5 shows the geometry of the sample and the reference and rastered point on the surface.

A KrF (248-nm photons) excimer laser (Questek 2860) was used for ionization in these experiments. The laser was power locked for 200 mJ/pulse and the experiments were run at 20 Hz. The ion beam current was 1.4 μ A. The laser beam size was reduced by apertures and collimated by two pairs of telescopes to a 1-mm $\times$ 3-mm spot in front of the target. The laser power (10 mJ/pulse) was monitored at the exit window of the experimental UHV chamber and was found to be unchanged during the experiments.

To compare the Fe and FeS₂ results, the Fe mass peaks were integrated and corrected for the detector gain. Although in most analyses of data from the SARISA apparatus, it suffices to use the peak height of the signal for comparison purposes, it was essential in this case to take into account the width of the mass peaks, since substantial differences were observed when comparing with RIMS spectra. As will be discussed in the later section, it appears that part of the NRIMS Fe signals from FeS₂ may not be from the sputtered atomic Fe. The signal

shape suggests that slower species such as photodissociated molecules are a possible source³¹ of some of the observed NRIMS Fe signal. The experimental results are shown in Fig. 4, where the ratio of the signal from the FeS₂ target to the signal from the Fe target versus the number of monolayers removed is plotted. This corresponds to the partial yield of Fe from FeS₂ as a function of the primary ion dose. There is high uncertainty in the primary ion dose in the LFS experiments and the result is not shown in Fig. 4. While the NRIMS signal ratio is higher than the one obtained by LFS and RIMS, it still saturates at 0.27, lower than expected from stoichiometry. These results will be discussed in detail in Sec. VI.

D. Profilometry measurements

Areas of 1 mm² on the FeS₂ and Fe samples were raster bombarded by a 3-keV Ar⁺-ion beam in the SARISA apparatus to form a (1–2)- μ m-deep crater. The samples were then sent to Charles Evans and Associates where the volume of the crater was measured by profilometry. The total number of FeS₂ molecules removed from the sample was calculated using the result of the profilometry measurements and the density of FeS₂. To calculate the yield, this number was divided by the total number of ions that bombarded the sample during formation of the crater. The sputtering yield for the Fe sample was calculated in a similar manner. The results of these measurements are presented in Table I. For high ion doses such as the profilometry experiment, steady-state sputtering is reached. Thus, if the sputtering process is assumed to be dominated by ejection of atomic species, then the partial yield of Fe from FeS₂ will be equal to the measured sputtering yield for FeS₂. Following this argument, the ratio R of the partial sputter yield of Fe from FeS₂ to the sputter yield of Fe from a pure Fe target can be obtained by ratioing the results of the profilometry measurements for the two samples. This ratio, defined to be the ratio of the yield of FeS₂ measured by profilometry to the yield of Fe measured by profilometry, or, equivalently, the ratio of the partial yield of Fe from FeS₂ to the yield of Fe from Fe,

$$R = 0.5 \pm 0.1,$$

TABLE I. Total yield measurements. Comparison of profilometry results and TRIM calculations, for 3-keV Ar⁺ normal-incidence bombardment, with the total yield measurements reported in the literature (Ref. 27). There is no reported measurement of total yield for FeS₂ in the literature. The yield is defined as the number of FeS₂ molecules sputtered (which correspond to one Fe atom) per primary Ar⁺.

Sample	Profilometry	TRIM	Literature
FeS ₂	1.1 $\pm$ 0.1	1.0 $\pm$ 0.4	
Fe	2.4 $\pm$ 0.15	2.2 $\pm$ 0.8	2.9

SCHEMATIC OF THE NRIS EXPERIMENTAL PROCEDURE

FIG. 5. A schematic view of the sample arrangement for the yield vs primary ion dose measurements. One millimeter below the center of the target was chosen as the reference point and was periodically checked to confirm the stability of the instrument transmission. The primary ion dose was applied by rastering a 1-mm $\times$ 1-mm area above the center of the target. Data were taken following each raster period.

indicates a substantially higher value than the partial yield ratios obtained from the LFS, RIMS, and NRIMS measurements with high ion dose.

IV. XPS MEASUREMENTS

The observation of similar velocity distributions for Fe from Fe and FeS₂ targets, as reported in Sec. II, poses an intriguing question as to whether islands of Fe form on the surface of FeS₂, due to preferential sputtering of S. This could also explain the low sputter yield of Fe from FeS₂ (Sec. III). To examine this possibility, the surface of the FeS₂ sample was probed using x-ray photoelectron spectroscopy (XPS) before and after ion bombardment. The FeS₂ sample, prepared in the same way as described in the previous section was examined using the XPS feature of the VGHB50A surface probe at Caltech. The required x rays were generated with a $K\alpha$ Al source, and an Ar⁺ beam of (5–6)-keV energy with $\sim(50\text{--}60)\text{-}\mu\text{A}/\text{cm}^2$ current was used to dose the sample.

While several different regions of photoelectron energy were scanned by XPS, the Fe(2*p*) and S(2*p*) are the most sensitive to changes in the chemical nature of the sample and were the focus of this study. Figures 6 and 7 show these two energy regions before and after ion bombardment, respectively. The spectrum of FeS₂ before sputtering shows some oxides on the surface as seen in Fig. 6.

FIG. 6. A partial XPS spectrum of FeS₂ before ion bombardment. (a) The narrow Fe(2*p*) peak at 707 eV is typical of FeS₂ and the change in the slope at 710 eV is indicative of oxide. (b) The S(2*p*) is at 164 eV, as expected. The ratio of the S peak to the Fe peak is approximately 0.17.

After 5 s of ion bombardment the oxide is removed and the surface is clean. The sample is then bombarded to a total fluence of 2.1×10^{18} ions/cm². The XPS spectrum after bombardment is shown in Fig. 7. The Fe(2*p*) peak at 707 eV in Fig. 6 is narrow and is typical of the electronic structure of FeS₂. The small change of slope around 710 eV is indicative of the presence of oxide. The S(2*p*) peak is at 164 eV. The peak signal ratio of S to Fe is ~ 0.17 . In Fig. 7, the Fe(2*p*) peak is now at 709 eV and the S(2*p*) peak is at 162 eV. In this case, the S-to-Fe peak signal ratio is ~ 0.10 . The shift in the electron binding energies of the two constituents indicates a change in the nature of their chemical bond. The ratios of Fe and S peaks in Figs. 6 and 7 were compared to the previously measured values.³² The surface of FeS₂ after ion bombardment resembles the more thermodynamically stable FeS surface. These results rule out the possibility of sputtering from islands of Fe on the FeS₂ surface that could explain our velocity distribution results. The XPS results further suggest that the yield of Fe from FeS₂ should be higher than observed from the detection of the secondary neutrals by laser spectroscopy. In addition, these results also confirm the profilometry measurements. The issue of the missing Fe will be discussed in Sec. VI.

FIG. 7. A partial XPS spectrum of FeS₂ after 2.5 h ion bombardment with 5-keV Ar⁺. (a) The Fe(2*p*) peak is now at 709 eV indicating the change in the chemical bonding in the near surface region. The signal level is higher than before bombardment. (b) The chemical bond shift is also apparent in the S(2*p*) peak, which is now at 162 eV and the signal level is the same as in Fig. 6. The ratio of the S peak to the Fe peak is 0.10.

V. TRIM CALCULATIONS

TRIM calculations were done to estimate the total sputtering yield from the target and the partial yield of the target constituents. TRIM is a Monte Carlo calculation that involves binary collisions, assuming an amorphous solid.¹⁹ At the high ion dose end of our measurements on FeS₂, the single crystalline effects are destroyed due to ion damage and the TRIM calculations can serve as a reference for the measurements. The sputtering products are assumed in these calculations to be limited to elemental Fe and S from FeS₂.

A. Yield calculations

Table I shows the total sputtering yield for FeS₂ as determined from the TRIM calculations, our profilometry results, and the values quoted from the literature.²⁷ The TRIM calculations required estimates of the surface binding energies of the two components, which are difficult to determine. Several different binding energies were chosen for S and Fe to better understand how they affect the yields. Results for binding energies for which the total yield obtained from the metal sulfide was more than from the pure targets were rejected. The results of some of these calculations are summarized in Table II.

B. Angular distribution calculations

The velocity distribution measurements of sputtered Fe from FeS₂ and Fe, as well as the XPS data and the profilometry measurements, suggest a higher Fe sputter yield from FeS₂ than observed from our NRIMS, RIMS, and LFS measurements. In order to understand this discrepancy, the angular distribution of Fe from the two targets was modeled using TRIM. These calculations simulate amorphous targets, and will not reveal any single-crystal effects that have been discussed by other groups.³³⁻³⁵ Because of this fact, the TRIM calculations are compared only with results obtained in the high-dose regime where single-crystal effects have been eliminated.

The angular distribution of sputtered Fe was obtained using the TRIM code for sputtering a 10⁴-Å-thick layer of FeS₂. This output is normalized to have a peak value of unity, and is plotted in Fig. 8(a) as a function of angle of ejection relative to the target surface normal. A cosine distribution of the ejection angle is also plotted in Fig.

8(a) for comparison. A second calculation was performed to simulate surface enrichment in Fe. An upper limit to this effect can be modeled by having a layer of Fe over FeS₂. In a separate TRIM run, a two-layer target was used where the first layer was 10 Å of Fe and the second layer was a 10⁴-Å-thick layer of FeS₂. These results are shown in Fig. 8(b). The results from the TRIM calculations show that both Fe and S are ejected from FeS₂ with the same angular distribution (which is slightly sharper than a cosine distribution). By adding a layer of Fe to the surface, the Fe angular distribution remains unchanged, but the sputtered S develops an over-cosine distribution even more sharply peaked toward the normal.

According to these calculations, the angular distribution of sputtered Fe is not different for Fe and FeS₂ targets. Since the instruments detection efficiency is the same for both cases, and sputtered Fe appears to have the same angular distribution, and considering the large angle of acceptance of the SARISA apparatus, any

FIG. 8. TRIM calculations of (a) angular distribution of sputtered Fe and S from FeS₂ target with amplitude normalized to unity (a cosine distribution is also plotted for comparison) and (b) angular distribution of sputtered Fe and S from FeS₂ target after prolonged bombardment (Fe enrichment in the surface has been simulated by placing a layer of Fe over the target).

TABLE II. TRIM yield calculations of FeS₂. Some of the results of the TRIM runs on FeS₂ showing the change in the yields for different surface binding energies (E_b). Cohesive energy of Fe and S for the elemental samples are 4.32 and 2.88 eV, respectively.²⁷ The ion beam energy used in all the calculations is 5 keV.

Fe E_b (eV)	S E_b (eV)	S yield	Fe yield
4.32	4.0	1.55	0.6
5.5	4.0	1.54	0.5
2.6	4.0	1.6	1.0
2.6	2.88	2.1	1.0

difference observed in the signal level is due to the difference in the sputtering yield.

VI. DISCUSSION

In Fig. 4 the RIMS and NRIMS measurements are plotted versus the primary ion dose in units of monolayers removed (10^{15} ions/cm²). In both sets of measurements, the partial yield of Fe starts from a very low value, and after removal of many monolayers of the FeS₂ target via ion bombardment, the partial yield saturates at a certain fraction of the Fe sputtering yield from a pure Fe target. This observation is due to the amorphization of the target or partial sputtering. By using the NRIMS technique, the partial yield of Fe is about 27% of $Y_{\text{Fe}}^{\text{Fe}}$ (sputtering yield of Fe from an Fe target), and in the RIMS measurement this number is about 19%. The RIMS results agree with the LFS measurements, since both of these techniques are state specific and only represent the partial yield of neutral ground-state Fe from FeS₂. The difference in the RIMS and NRIMS signal level ratios could be due to the differences in the excited-state population distribution from the two targets. If sputtered Fe from a FeS₂ target has a higher population in metastable states, then the NRIMS signal level will be higher than the RIMS signal level. This possibility was also suggested by Husinsky *et al.*³⁶ to explain the lower than expected neutral atomic yield from Cr compounds, which they observed. The population distribution of Fe ground multiplet states was measured for the two targets and is described in detail in a separate paper.³⁷ Briefly, we found that the ground-state fraction of the sputtered Fe was 10% lower for FeS₂ than for the Fe target. By taking into account this slight difference in the fraction of ground-state sputtered Fe from the two targets, the saturation level of the partial yield measured by RIMS will be 22%. Another possibility for the RIMS and NRIMS difference is the generation of Fe from photodissociated molecules into metastable levels that remain undetected by the RIMS method.

The more significant finding from our data is that, while the high-dose partial yield for Fe from a FeS₂ target as determined by LFS, RIMS, and NRIMS are all internally consistent, they differ substantially from the value measured by profilometry assuming steady-state sputtering and stoichiometric yields. According to our profilometry measurements reported in Table I, the ratio of the Fe partial yield from an FeS₂ target to that yield from a pure Fe target is $R = 0.5 \pm 0.1$. This is especially interesting in light of the similar surface binding energy of Fe, which we observe for the FeS₂ and Fe targets. The lower yield that is measured in the sputtered neutral den-

sity experiments pose the question as to whether all of the Fe sputtered from FeS₂ is detected by our laser-based techniques. As discussed above, the angular distribution calculated by TRIM did not show any difference for the sputtered Fe from the two targets suggesting that the detection efficiency of the instrument remains the same. According to our XPS measurements, while some excess Fe remains on the surface during sputtering, steady-state conditions are established. This result in combination with the profilometry measurements confirms the expectation of a stoichiometric partial sputtering yield for Fe from FeS₂. Our explanation for the lower than expected laser-based Fe signal is that the Fe is sputtered in forms that even the nonresonant technique is not ionizing efficiently. There are, of course, some molecules that are not photodissociated³¹ or are not ionized after photodissociation. This could account for the difference in the signal ratio saturation level obtained by RIMS and NRIMS and the profilometry measurements.

VII. CONCLUSIONS

We have examined the sputtering of Fe from FeS₂ by means of detecting secondary neutrals as well as probing the ion bombarded surface. Quantitatively, the velocity distribution of Fe from a heavily dosed FeS₂ target is very similar to that from an Fe target and follows a Sigmund-Thompson distribution. The maximum of the Fe velocity distribution for the sulfide and the metal targets is very similar. The neutral atomic yield of Fe from a heavily dosed FeS₂ is about 27% of the Fe yield measured in the same apparatus from an Fe target. From our XPS measurements, it is concluded that the Fe does not concentrate as islands on the surface and is sputtered from an FeS target. The reason for the difference in the yield as determined by laser-based measurements and from profilometry results occurs is most likely due to Fe being sputtered in forms that escape our detection, possibly as molecules (such as FeS)³¹ and clusters.

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FIG. 3. A schematic of the experimental layout in the SARISA apparatus. The detection angle is determined by the distance of the laser from the target and the transmission characteristics of the ion optics (Ref. 29).

SCHEMATIC OF THE NRIS EXPERIMENTAL PROCEDURE

FIG. 5. A schematic view of the sample arrangement for the yield vs primary ion dose measurements. One millimeter below the center of the target was chosen as the reference point and was periodically checked to confirm the stability of the instrument transmission. The primary ion dose was applied by rastering a 1-mm $\times$ 1-mm area above the center of the target. Data were taken following each raster period.