Formation mechanism and yield of molecules ejected from ZnS, CdS, and FeS₂ during ion bombardment*

S. Nikzad**, W.F. Calaway, M.J. Pellin, C.E. Young, and D.M. Gruen
Materials Science, Chemistry, and Chemical Technology Divisions
Argonne National Laboratories
Argonne, IL 60439

T.A. Tombrello
Division of Physics, Mathematics, and Astronomy
California Institute of Technology
Pasadena, CA 91125

JUL 21 1974

Abstract

Neutral species ejected from single crystals of ZnS, CdS, and FeS₂ during ion bombardment by 3 keV Ar⁺ were detected by laser post-ionization followed by time-of-flight mass spectrometry. While metal atoms (Fe, Zn, Cd) and S₂ were the dominant species observed, substantial amounts of S, FeS, Zn₂, ZnS, Cd₂, and CdS were also detected. The experimental results demonstrate that molecules represent a larger fraction of the sputtered yield than was previously believed from secondary ion mass spectrometry experiments. In addition, our data suggest that the molecules are not necessarily formed from adjacent atoms in the solid and that a modified form of the recombination model could provide a mechanism for their formation.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

* Work supported by the US Department of Energy, BES-Materials Science, under contract W-31-109-ENG-38

** Present address: Department of Applied Physics, Caltech, Pasadena, CA 91125

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ok*

I. Introduction

Although sputtering of atoms from metal targets has been the subject of extensive research in the past three decades, the understanding of molecular sputtering mechanisms is in an early stage.¹ Clearly, the sputtering of molecules is much more complicated than that of atoms because dynamics of molecular formation and dissociation influence the existence and abundance of molecular species produced during ion bombardment. In addition, it is uncertain whether single collisions produce molecular sputtering. Theoretical endeavors in this area have focused on extending to molecules the cascade model that has been successfully applied to atomic sputtering.²⁻⁶ These models can be divided into two major categories. In the direct emission models, sputtered molecules originate from atoms that are adjacent and associated in the solid.^{2,4,7} In recombination models, molecules are formed above the surface,^{3,8} and thus are not constrained by location or prior association in the solid. In both classes of models, ejection can occur either through a single collision or simultaneous multiple collisions. Molecular dynamics calculations of sputtered molecules, performed primarily by Garrison and Winograd, support the recombination model.^{8,9}

Only a limited number of experimental studies have focused on molecular sputtering results. With the exception of a few experiments,¹⁰⁻¹⁶ most of these studies measured either sputtered molecular ions with secondary ion mass spectrometry (SIMS)⁷ or sputtered molecules in excited states by observing optical emission.^{17,18} While these measurements are of some use in guiding theoretical developments, they are results of probing only the ions and excited molecules which are not the majority of molecules in the sputtered flux. Secondary neutral mass spectrometry (SNMS) coupled with post laser ionization has been demonstrated as an efficient method for studying the neutral flux during ion bombardment.^{14-16,19-21} Using the SNMS instrument developed and built at Argonne National Laboratory, we have begun a comprehensive experimental

study of molecular sputtering in order to understand the nature of molecular ejection from surfaces during ion bombardment.

Recent studies from our laboratory reported on the yield and energy distribution of molecules from polycrystalline Cu.¹⁴ While these experiments differentiated between single and multiple collision mechanisms, the yield and energy distribution data from a single constituent sample cannot easily distinguish direct emission from recombination mechanisms of molecular sputtering. With no conclusive experimental results, the relative importance of direct emission and recombination in molecular sputtering remains an open question. Differentiation between these two mechanisms can be addressed by sputtering experiments using a binary target, in which the constituents of the sputtered molecules do not occupy nearest neighbor sites in the crystal. We have conducted a study on three single crystal metal-sulfides having two different lattice structures. Using SNMS and nonresonant photo-ionization, along with profilometry measurements, the relative yields of various molecular species have been estimated. From the data, we find that the dominant mechanism for formation of molecules is a modified form of the recombination mechanism.

To accurately measure the absolute yields of sputtered neutrals, it is necessary to ionize 100% of the ejected species, as determined by saturation of the laser-ionized signal. Laser-induced dissociation of molecules (photo-fragmentation) is known to reduce the measured yield of most molecules. Furthermore, the photo-fragmented molecules can contribute to the monomer signal. To minimize this problem, each species can be detected by RIMS (resonance ionization mass spectrometry) where a separate measurement is required for each species. However, resonant measurements require spectroscopic information for all of the observed molecules, which are not always available. The NRIMS technique has the advantage of detecting signals from all molecular and atomic species simultaneously. Since the sputtered species have different ionization efficiencies and cross sections, simultaneous saturation of all signals is not easily accomplished with the NRIMS technique. For monomers, the laser power density

required for saturating a transition can be easily determined by studying signal variations with increasing laser power density. For molecular sputtering, however, saturation is complicated by photo-fragmentation of the molecules by the laser. To address photo-fragmentation of molecules, and to assess its effect on the measured yields, variation of the signal with excimer laser power density was studied for the detected species.

II. Experimental

The experiments described in this paper were performed using an energy and angular refocusing time-of-flight mass spectrometer specially designed for laser post ionization.²² A pulsed 3 keV Ar^+ beam ($1.5 \mu\text{A}$, 400 nsec) strikes the target at normal incidence, causing ejection of atoms, molecules, and clusters. A fraction of the secondary neutrals are ionized by a laser beam propagating parallel to the surface of the sample, extracted in the time-of-flight mass spectrometer, and measured by a chevron microchannel plate detector, as shown in Figure 1. In these experiments, a multiphoton nonresonant ionization scheme was employed, primarily utilizing an ArF excimer laser (6.4 eV photons, 20 nsec pulse). Some measurements were also performed with a KrCl laser (5.6 eV photons) in an attempt to study the effect of photon energy on the photofragmentation of molecules. In both cases, the laser was operated in a constant power mode at 40-50 Hz. The ArF beam was collimated and focused to a $0.1 \text{ mm} \times 3 \text{ mm}$ cross section intersecting the path of the sputtered species and the KrCl beam was focused to $1 \text{ mm} \times 3 \text{ mm}$ spot. For high laser powers, where the signal to noise ratio was high, the signal from the detector was charge digitized. At lower laser powers, individual pulse counting was employed. In both the charge-digitized and the pulse counting modes, the signal was typically averaged over 10^4 laser shots.

The single crystal targets were used in these experiments. The CdS and ZnS were synthetically grown and have the Wurtzite structure, while the FeS_2 (pyrite) was a natural crystal with the cubic structure. The FeS_2 samples were cut from the

natural crystal with a diamond saw and were ultrasonically cleaned with trichloroethylene, acetone, and methanol before insertion in the UHV chamber. Acetone and methanol were used for cleaning CdS and ZnS.

To assess the degree of ionization saturation and photo fragmentation, power studies were conducted on all observed sputtered species. In these power studies, the laser power was varied by the attenuation with a series of glass plates. Power densities were calculated by dividing average laser power measured at the exit window of the UHV chamber divided by the laser cross section as measured from burn spots made by the laser at an equivalent focus point outside the UHV chamber (Fig. 1). Results of the power studies are presented in plots of the dimer signal relative to the saturated monomer signal as a function of the laser average power density.

We have also measured total sputtering yields from the three metal sulfides and from Zn and Fe elemental targets. The samples were sputtered using the same Ar^+ beam employed for the other experiments, operating the beam continuously and rastering in a 1 mm x 1 mm area for a period of 1-2 hours to produce a crater a few microns deep. The total amount of material removed was estimated from the density of the material and the crater volume, measured by profilometry at Charles Evans and Associates. Using this data, the total sputtering yields for the compounds were calculated in terms of the equivalent number of metal sulfide molecules (ZnS , CdS , and FeS_2) removed per impinging Ar^+ ion.

III. Results of NRIMS power studies

Ionization potential (IP) of the observed monomers and molecules are listed in Tables 1 and 2 respectively. Ionization potential data are not available for some of the observed molecules in sputtering ZnS , CdS , and FeS_2 , but assuming that the diatomic molecules' IP does not vary drastically from that of the monomers, all species sputtered from ZnS , CdS , and FeS_2 targets have ionization potentials that

exceed the ArF and KrCl photon energies, and are ionized by absorbing two photons.

In the ion bombardment of ZnS, we have observed the ejection of neutral S, S₂, Zn, ZnS, and Zn₂ ionized by the ArF laser. Because of an isobaric interference between ³²S₂ and ⁶⁴Zn, the known relative abundance of Zn isotopes were used to extract the S₂ signal from the measured signal at 64 amu. At the highest laser power (~ 50 W/cm²) density used, the signals detected at 64, 66, and 68 amu corresponded to the natural abundance of the three Zn isotopes ⁶⁴Zn, ⁶⁶Zn, and ⁶⁸Zn. This indicates that all sputtered ³²S₂ was photo-dissociated at this laser power density. As the laser power density was reduced, the ratio between the signals at 66 and 68 amu remained constant, while the ratio between the signals at 64 and 66 amu increased. This is interpreted as the detection of both ⁶⁴Zn and ³²S₂ at 64 amu at lower laser power densities. The ⁶⁴Zn signal was extracted by multiplying the ⁶⁶Zn signal by the natural abundance ratio. The remainder of the signal at 64 amu was assigned to ³²S₂, and was normalized to the S signal. Variation of this normalized signal with ArF laser power density is shown in Figure 2. The ³²S₂ signal increases with increasing laser power, indicating that the ionization is not saturated. The signal remains constant for a small range of laser powers and declines for higher laser powers, confirming that at higher laser powers, the dimer is photo-dissociated.

ZnS and Zn₂ were also observed to be ejected from the ZnS target during ion bombardment. The Zn dimer has been observed by others as an excimer, but never in the ground state.²³ Since the ground state Zn₂ has very low binding energy (Table 1), we believe that the Zn₂ observed in our experiments is also in an excited state. The ZnS molecule is also weakly bound. It has been observed in the gas phase in Knudsen cell experiments on ZnS crystal.²⁴ Figure 3 depicts as a function of the laser power density, the signal of these molecules relative to the saturated Zn signal, calculated using the peak height corresponding to ⁶⁴Zn atom and corresponding molecules. Signal at mass 132 amu is made of contributions from ⁶⁶Zn₂ and ⁶⁴Zn⁶⁸Zn dimers. Natural isotopic abundance was used to extract from

signal at mass 132 amu that corresponds to the dimer formed by ^{64}Zn and ^{68}Zn to account. The maximum observed normalized signals for Zn_2 and ZnS ~ 0.05 .

Ion bombardment of CdS was also examined. Isobaric interference was not a problem in measurements of sputtering from CdS . This material has the same crystal structure as ZnS , but the mass of Cd is ~ 114 amu, thus eliminating isobaric interference that masks the $^{32}\text{S}_2$ from ZnS . The S_2 observed from sputtering of CdS is normalized to the saturated S signal and plotted in Figure 2 as a function of the ArF laser power density. The normalized S_2 to S signal is greater than 1 for the range of laser power densities studied ($2\text{--}13\text{ W/cm}^2$). The signal from the CdS molecule is not very strong, and the experimental conditions precluded the detection of the Cd_2 dimer. On the average, the relative signal of CdS to the saturated Cd signal is about 0.02.

In separate experiments a KrCl laser, which has lower photon energy and less power density, was used to ionize the sputtered species from a CdS target to lower the probability of molecular photofragmentation. By ionizing the sputtered species with 5.6 eV photons from the KrCl laser, we detect a strong Cd monomer signal. By electronically blocking the Cd signal to avoid saturating the detector, we were able to detect Cd_2 , CdS , and CdS_2 . The signals obtained from these species were at most 2% of the saturated Cd monomer signal. Of the sputtered molecular species with Cd as a constituent, the Cd_2 signal was the strongest, followed in relative intensity by CdS and CdS_2 . The relative S to Cd signal is ~ 0.24 at the same laser power density where CdS , Cd_2 and CdS_2 were observed ($7\text{--}50\text{ W/cm}^2$). The same qualitative trends in the change of the dimer signals from a ZnS target as a function of laser power density were observed in sputtering from a CdS target.

A laser power study was also performed employing the ArF laser to ionize the neutrals ejected from ion-bombarded FeS_2 . We observed signals corresponding Fe , S , S_2 , and FeS . No Fe_2 was detected in these experiments. Figure 4 shows variations of FeS signal, normalized to the saturated Fe signal using the peak heights from saturated ^{56}Fe signal, with ArF laser power density. The normalized

FeS signal exhibits a weak dependence on laser power density and had a maximum of 0.015 at intermediate laser power density ($\sim 15 \text{ W/cm}^2$). The normalized S_2 signal to saturated S signal, plotted as a function of the laser power density in Figure 5, shows the same qualitative trend as the data from the CdS and ZnS targets (Figure 2). At intermediate laser power density, the S_2 signal was observed to be twice the saturated S signal. Ratio of the saturated S signal to the saturated Fe signal was 0.006.

For all targets studied, the normalized signal from diatomic molecules to increases with laser power density up to some intermediate power, then decreases as the laser power is further increased. This is interpreted as competition between saturation of the ionization and photo-fragmentation of the molecules, providing a dividing line between low and high power regimes of laser ionization of a molecular species for quantitative yield analysis. This is demonstrated in saturation of sputtered S signal from the three metal sulfides as depicted in Fig. 6 a, indicating that the variations in the S_2 signal (in Figs. 2 and 5) is due to photofragmentation of the dimer as well as its photo-ionization. Figure 2b shows the variations of the S signal and S_2 signal with laser power density. The S signal is saturated but the S_2 signal decreases with increasing laser power density presumably due to photofragmentation of the dimer.

Formation mechanisms of molecules

In this section we will discuss how our measurements can be used to determine the dominant mechanism for the formation of molecules due to ion bombardment. Information on the dissociation energies and the ionization potentials of the dimers, summarized in Table 1, will be used to interpret our observations in the context of existing theories.

In bulk ZnS and CdS, only metal-sulfur bonds are present. In the case of FeS_2 , only S-S and Fe-S bonds exist. Thus, the presence of the molecules Zn_2 , Cd_2 , and S_2 in the mass spectra suggests that these sputtered molecules form either above the

solid surface after being ejected due to ion bombardment, or they form in the solid as a result of cascade collisions. In ion sputtering, the flux of generated particles above the surface is in general small/compared to laser ablation.^{25,26} Most models for formation of molecules above the target surface invoke some form of three-body interaction is necessary after the dimer constituents have been ejected from the surface through separate collisions (the so-called double collision model). Other possible interactions responsible for recombination of the constituents are charge transfer to the surface and photon emission.²⁷ However, the photon emission probabilities are low and secondary molecular ions are in general minor constituents. For these reasons, dimer formation in the target followed by ejection via single collision or simultaneous double collisions is a more plausible mechanism. Given the structure of the targets in this study, more than a single collision is necessary to form the observed dimers. We will refer to this as the modified recombination process. A similar process has also been suggested by Garrison²⁸ in a theoretical study of cluster formation in noble gas matrices by keV ion bombardment.

A significant finding supporting molecular formation in the target was the observation of molecules before and after prolonged ion bombardment of the CdS sample. Results of measurements conducted after an ion dose of 1.6×10^{16} ions/cm² were identical to measurements on the virgin surface at the same laser power density. According to previous measurements,^{29,16} this ion dose is sufficient to destroy the crystallinity of the target surface. This suggests that a modified recombination process (occurring on the sample surface) requires only a small ion dose. Even though most of our experiments were done in the static mode, because of the arguments above, We believe that, due to the violent nature of the sputtering process, rearrangement of the atoms to form molecules occurs in each cascade. These molecules are then ejected according to their binding energy to the surface, and are detected if they are not dissociated.

Our data are qualitatively consistent with the theory² that survival of the molecule depends on the dissociation energy and the binding energy of that molecule to the surface. To interpret our results, we examine the dissociation energies and surface binding energies of the molecules. The photo-dissociation energies for ground state Zn_2 and Cd_2 are 0.09 eV and 0.168 eV respectively, as shown in Table 1, but these molecules are more strongly bound as excimers. In the simplest approximation, the binding energy of a molecule is assumed to be equal to the sum of the surface binding energies of the constituent atoms, and an atom's surface binding energy is estimated by the elemental sublimation energy, shown in Table 2.³⁰ It is conceivable to think of the metal sulfide as being more strongly bound to the surface than the metal dimers of Cd and Zn. This is one possible explanation for our observation of stronger signals for Cd_2 and Zn_2 than for CdS and ZnS. This approximation is consistent with the larger signal level of S_2 and metal dimers (Cd_2 and Zn_2) than metal-sulfide molecules (CdS and ZnS), as observed in our experiments. Cd and Zn have smaller surface binding energies than S.

Consistent with this argument is the detection of FeS in our experiments, and the absence of an Fe_2 signal. The Fe_2 surface binding energy is ~9 eV (twice that of Fe for elemental target)³¹ compared to ~7 eV for FeS (sum of Fe and S surface binding energy for elemental targets). The dissociation energies of FeS and Fe_2 are 3.3 eV and 1.1 eV, respectively (Table 1). Thus, the Fe_2 molecule is harder to eject and easier to break during ejection compared to FeS. These trends suggest an important relationship between molecular binding energy, surface binding energy, and sputtering yields. Resonant experiments measuring the molecular energy distribution (kinetic and internal) would be useful to quantify these relationships.

The yield of molecules from ZnS, CdS, and FeS_2

Although all of the species required a two photon ionization process, the various sputtered species have different ionization efficiencies. The ionization

cross section varies for different species and decreases with the number of photons needed for ionization. In our measurements, the instrument was optimized to detect the sputtered metal monomer signal and this signal was saturated. To assess the molecular yield from any sample, comparisons should be made between saturated signals from the monomers and dimers. An estimate of the yield can be made by saturating the monomer signal and taking the ratio of the dimer signal to saturated monomer signal. Table 3 shows the ratio of the maximum dimer signal to the saturated metal signal from each target. Because these measurements are nonresonant and the photo-fragmentation of the dimers could contribute to the monomer signal, the values in Table 3 serve as a lower bound for the molecular yield from these compounds.

Table 4 lists the total yields obtained from profilometry measurements on compound and elementary targets. These results are listed with the values existing in the literature.^{32,33} Compared to the NRIMS data, profilometry total yield measurements offer limited information. However, measurements of the total yield are useful to quantify the partial yields of the constituents of the compound. By using these total yields along with partial yields estimated from NRIMS data, we can begin to quantify the NRIMS data. For example, the total yield of ZnS shown in Table 4 is calculated as the equivalent of sputtering ZnS molecules. Assuming sputtering products are dominated by monomer ejection, the partial sputtering yield of Zn is the same as the total sputtering yield of ZnS. Moreover, using the normalized dimer signal to the saturated monomer signal (Table 3) for Zn₂ to estimate the partial yield would give:

$$\begin{aligned}
 y(\text{Zn}_2) &= k \times S_n(\text{Zn}_2) \times y(\text{Zn}) \\
 &= k \times S_n(\text{Zn}_2) \times Y(\text{ZnS}) \\
 &= k \times 0.045 \times 2.5 \\
 &= k \times 0.11
 \end{aligned}$$

where $y(\text{Zn})$ and $y(\text{Zn}_2)$ are the partial yields of Zn monomer, Zn_2 , $Y(\text{ZnS})$ is the total yield of ZnS, $S_n(\text{Zn}_2)$ is the normalized Zn_2 signal to the saturated Zn monomer signal, and k is a constant defined as $k = \frac{I(\text{Zn}_2)}{I(\text{Zn})}$ where $I(\text{Zn}_2)$ and $I(\text{Zn})$ are the dimer and monomer ionization efficiencies respectively. In the case of the saturated monomer the numerator for k is one and $k > 1$.

Comparisons with previous SIMS studies

Much of the existing data on the molecular sputtering yield comes from SIMS studies. However, the neutral dimers seem to form the majority of the sputtered dimers, as is true for the monomers. To demonstrate this, we compared the results of this work with previous SIMS studies on metal sulfides. In SIMS measurements performed on thin film ZnS,³⁴ secondary ions of ZnS^+ and Zn_2^+ were not observed. Moreover, all of the signal at mass 64 amu was attributed to Zn^+ since the ejection of S_2^+ was deemed unlikely.³³ In a SIMS study of single crystal FeS_2 ,³⁵ positive ions of S, Fe, S_2 , FeS, Fe_2 , FeS_2 , Fe_2S , and Fe_2S_2 were observed. The negative ions observed were S, S_2 , and FeS_2 . The largest signal in the positive ion yield belongs to atomic Fe^+ and the smallest is S_2^+ . Since the ionization efficiencies of the different species are not the same, these SIMS were not quantitative comparative analyses.

While in the NRIMS technique the ionization efficiency is also species dependent, we are detecting the majority (neutral species), and, therefore, getting a better picture of the sputtering mechanism.

Summary and Conclusions

In sputtering metal sulfides with different crystal structures, we have observed sputtered molecules with constituents that do not have a preexisting bond in the solid. Thus, these molecules must be formed in the sputtering process

itself, suggesting that some form of recombination mechanism (inside or outside the solid) is responsible for the formation of molecules. There are more sputtered metal atoms than metal dimers, whereas S is predominantly sputtered as S_2 from all three samples. Our data also show that the sputtered molecules form a measurable fraction of the sputtered species. Therefore, a quantitative analysis is important to obtain an accurate measure of molecular sputtering yields.

Acknowledgments

We thank M.E. Hoenk and J.W. Burnett for many helpful discussions. This work was supported by the US Department of Energy, BES-Materials Science, under contract W-31-109-ENG-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

1. P. Sigmund in, *Sputtering by Particle Bombardment I*, edited by R. Behrisch, (Springer-Verlag, Berlin Heidelberg New York Tokyo 1981), p 9.
2. K.J. Snowdon, R. Hentschke, W. Heiland, and P. Hestel, *Z Phys. A-Atoms and Nuclei* **318**, 275 (1984).
3. P. Sigmund, H.M. Urbassek, and D. Matragrano, *Nucl. Instrum. Methods* **B14**, 495 (1986).
4. H. M. Urbassek, *Nucl. Instrum. Methods* **B18**, 578 (1987).
5. W. Gerhard, *Z. Phys.* **B22**, 31(1975).
6. R.A Haring, H.E. Roosendaal, and P.C. Zalm, *Nucl. Instrum. Methods* **B28**, 205 (1987).
7. R. Buhl and Preisinger, *Surf. Sci.* **47**, 344 (1975).
8. B.J. Garrison, N. Winograd, D.E. Harrison, Jr., *J. Chem Phys.* **69**, 1440 (1978).
9. N. Winograd, K.E. Foley, B.J. Garrison, and D.E. Harrison, Jr., *Phys. Lett.* **73A**, 253 (1979).
10. R. De Jonge, K.W. Bensist, J.W. Major, A.E. De Vries, and K.J. Snowdon, *Nucl. Instrum. Methods* **B28**, 214 (1987).
11. W. O. Hofer and H. Gnazer, *Nucl. Instrum. Methods* **B18**, 605 (1987).
12. H. Oechsner and W. Gerhard, *Surf. Sci.* **44**, 481 (1974).
13. R. Hoogerbrugge and P.G. Kistemaker, *Nucl. Instrum. Methods* **B18**, 600 (1987).
14. S.R. Coon, W.F. Calaway, J.W. Burnett, M.J. Pellin, D.M. Gruen, D.A. Spiegel, and J.M. White, *Surf. Sci.*, 259, 275 (1991).
15. S. Nikzad, W.F. Calaway, C.E. Young, M.J. Pellin, D.M. Gruen, and T.A. Tombrello, *Materials Research Symposium Proceedings*, **201**, 93 (1991).
16. S. Nikzad, W.F. Calaway, C.E. Young, M.J. Pellin, D.M. Gruen, T.A. Tombrello, and R.M. Housley, *Phys. Rev. B* **45**, 10255 (1992).
17. E.A. Thomas and L. Efstathiou, *Nucl. Instrum. Methods* **B2**, 479 (1984).
18. K.J. Snowdon and W. Heiland, *Z. Phys. A* **318**, 275(1984)
19. J.W. Burnett, W.F. Calaway, C.E. Young, M.J. Pellin, D.M. Gruen, and J.T. Yates, *Phys. Rev. Lett.*, **63**, 562, (1989).
20. M. El-Maazawi, R. Maboudian, Z. Postawa, and N. Winograd, *Phys. Rev. B*, **43**, 12078, (1991).

21. R. Maboudian, Z. Postawa, M. El-Maazawi, B.J. Garrison, and N. Winograd, *Phys. Rev. B*, **42**, 7311 (1990).
22. M.J. Pellin, C.E. Young, D.M. Gruen, *Scanning Microsc.* **2**, 1353 (1988).
23. W. Kedzierski, J.B. Atkinson, and L. Krause, *Optics Lett.* **14**, 607 (1989).
24. M. Grade and W. Hischwald, *Z. Anorg. Allg. Chem.* **460**, 106 (1980).
25. P.D. Brewer, J.J. Zink, and G.L. Olson, *Mat. Res. Soc. Symp. Proc.* **191**, 67 (1990).
26. H.F. Arlinghaus, W.F. Calaway, C.E. Young, M.J. Pellin, D.M. Gruen, and L.L. Chase, *J. Appl. Phys.* **65**, 281, (1989).
27. K. Snowden, *Nucl. Instrum. Methods B9*, 132 (1985).
28. B.J. Garrison and N. Winograd, *Chem. Phys. Lett.*, **97**, 381 (1983).
29. A. Johansen, E. Johnson, L. Sarholt-Kristensen, and S.M. Abdali, *Nucl. Instrum. Methods* **218**, 737 (1983).
30. N. Matsunami, Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu, and H. Tawara, *At. Data Nucl. Data Tables* **31**, 1 (1984).
31. In reference 16 we have measured the surface binding energy of Fe to an FeS₂ target to be very similar to that from a pure Fe target.
32. H.H. Andersen and H.L. Bay, in, *Sputtering by Particle Bombardment I*, edited by R. Behrisch, (Springer-Verlag, Berlin Heidelberg New York Tokyo 1981).
33. G. Betz and G.K. Wehner, *Sputtering by Particle Bombardment II*, edited by R. Behrisch, (Springer-Verlag, Berlin Heidelberg New York Tokyo 1983).
34. A. Aoki, *Jap. J. Appl. Phys.* **19**, 1901 (1980).
35. M.A. Karolewski and R.G. Cavell, *Surf. Sci.* **210**, 175 (1989).
36. A.A. Radzig and B.M. Smirnov, *Reference Data on Atoms, Molecules, and Ions*, (Springer-Verlag, Berlin, 1985).
37. S.W. Buckner, J.R. Gord, and B.S. Freiser, *J. Chem. Phys.* **88**, 3678 (1988).
38. A.G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, (Chapman & Hill, London, 1968).

Molecules	D (eV)	IP (eV)
Cd ₂ ³⁶	0.09	----
CdS ³⁷	3.9±0.3	----
Fe ₂ ³⁶	1.1 (C)	----
FeS ³⁶	3.3 (C)	----
FeS ₂	-----	----
Zn ₂ ³⁸	0.168	9.2±0.2
ZnS ³⁶	2.1 (C)	-----
S ₂ ³⁶	4.4 (A)	9.4

Table 1 The ionization potential (IP) and dissociation energies (D) are the relevant parameters in the formation of molecules during sputtering. The letters A, C, and D mean 1%, 10%, and 30% accuracy in the measurements, respectively, for data from Radzig³⁶. The blanks in the table represent values not found in the literature. The ionization potentials and dissociation energies of CdS and Zn₂ were reported by other sources.^{37,38}

<u>Element</u>	<u>Sublimation Energy (eV)</u>	<u>IP (eV)</u>
S	2.88	10.36
Fe	4.34	7.9
Cd	1.16	8.99
Zn	1.35	9.39

Table 2 The sublimation energies³⁰ and dissociation energies D^{36} of the elements in the compound used in this study are listed above. According to sputtering theory for elemental targets, surface binding energy of an atom to an elemental target is estimated by the sublimation energy of that element, which is inversely proportional to the sputtering yield of the element.

Sputtered species to saturated metal monomer ratio	Lower bound ratio
Zn_2/Zn	0.05
ZnS/Zn	0.06
Cd_2/Cd	0.02
CdS/Cd	0.02
FeS/Fe	0.03

Table 3. The lower bound for the yield of dimers. These numbers were calculated by the ratio of the dimer signal maxima at an intermediate laser power density to the saturation level of the sputtered metal signal.

Total Yield Measurements

Sample	This Study	Literature ^{30,32}
Fe	2.4	3.1
FeS ₂	1.5	-----
Zn	18	15
ZnS	1.4	2.5
Cd	-----	20
CdS	2.8	-----

Table 4. The samples were raster-sputtered by 3 keV Ar⁺ with 1 to 2 μ A of current. The volume of the crater formed by ion bombardment was then measured by profilometry to determine the amount of material removed in sputtering.

Figure Captions

Figure 1: Schematic of the experimental setup. The laser, which is focused in front of the sample, is timed so that the pulse arrives after the ion beam has impinged on the target causing ejection of atoms and molecules. A fraction of the ejected neutrals are ionized and are detected after traveling in the time of flight mass spectrometer.

Figure 2: a). Variations of the normalized sputtered S_2 signal to the S signal from ZnS and CdS with average power density of the ArF laser. Photo-dissociation of the molecules at higher laser power density causes the decline in the signal.

Figure 3: Normalized ZnS and Zn_2 signals to the saturated Zn signal in sputtering a ZnS target are plotted as a function of the laser power density. Sputtered Zn from a ZnS target was observed in atomic form as well as Zn_2 and ZnS molecules. ZnS has a higher dissociation energy than Zn_2 and is observed at higher laser power.

Figure 4: Normalized FeS signal to the saturated Fe signal as a function of laser power density in sputtering of an FeS_2 target. Higher laser power densities cause fragmentation of the molecule, as shown in Figure 2. The ionization potential and dissociation energies of the various molecules are the competing factors in the survival and observation of the species.

Figure 5: Normalized S_2 signal to the S signal variation with laser power density in sputtering of FeS_2 exhibits the same qualitative features as sputtering of S from CdS and ZnS targets shown in Figure 2.

Figure 6: a) Variations of S monomer and dimer sputtered from CdS target and ionized with ArF laser. c) Saturation of S monomer from the three metal sulfides with the ArF laser. The signals are normalized to the same value at high laser power density to observe the saturation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

An alternate Fig 6b.

DATE

FILMED

4 / 13 / 94

END