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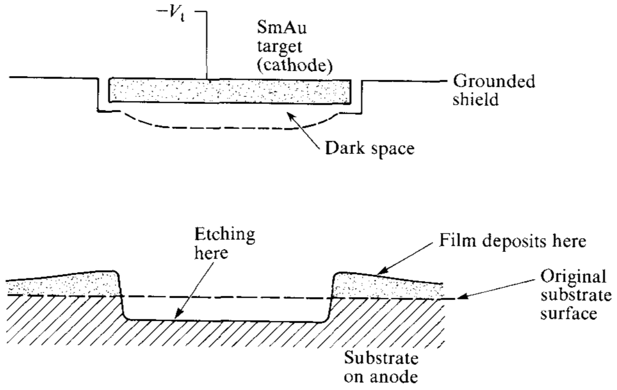
Origin and Effects of Negative Ions in the Sputtering of Intermetallic Compounds

Abstract: An unexpected etching phenomenon during the sputtering of rare earth-gold alloys has been found to be caused by a large flux of negative gold ions from the sputtering target. We find this effect to occur in a range of intermetallic compounds. A model is presented which predicts when negative ion formation will be important. Effects of negative ions on sputter deposition of thin films include reduced deposition rate or substrate etching, and changes in film composition and other properties. Negative ion formation must also be taken into account for accurate quantitative analysis by Secondary Ion Mass Spectrometry (SIMS).

Introduction

The formation of negative ions in the sputtering of highly ionic compounds such as TbF_3 has been reported by Hanak [1]. In this communication we present experimental data which show that negative ion formation has a significant effect on the sputtering of certain intermetallic compounds and not just the highly ionic compounds previously reported [1]. In addition we present a model based on electron affinity data [2] which is useful in predicting the compounds and intermetallics that will have a high negative ion yield. In the normal use of sputtering for thin film deposition, bombardment of the target by energetic ions results in the ejection of mainly neutral species, which are collected on substrates in thin film form. With the compounds discussed here, however, a large flux of negative ions is ejected from the target. This can drastically affect the properties of the growing film, to the extent of completely suppressing film deposition and actually etching the substrates. This finding also has important implications for analysis of these materials by Secondary Ion Mass Spectrometry (SIMS), in which quantitative analysis will be in error if the yield of negative ions is not taken into account.

Figure 1 Sketch of rf sputtering configuration showing regions of substrate etching and film deposition. Target voltage V_t ranges from 500 V to 2500 V, and the substrate is at the anode voltage of −50 V.



The influence of negative ions on the sputtering process came to our attention during the sputter deposition of a series of rare earth-gold alloys. For most compounds of the series, normal film deposition occurs. For SmAu, however, the area directly under the sputtering target shown in Fig. 1 has no film accumulation and the substrates placed on the anode are actually eroded, or etched. Outside this region film deposition occurs. The etched area closely matches the shape of the grounded shield surrounding the sputtering target, and the etching occurs for several types of substrates (Si, glass, Al_2O_3, and Mo), showing no evidence of being a chemical etching phenomenon. This etching is not to be confused with normal sputter-etching in which the substrates are placed on the target surface, which is held at a high negative voltage to cause bombardment by positive ions of the sputtering gas. In our experiments the substrates are located on the anode, which is held at a low negative bias voltage of about 50 V such that positive ion bombardment of the substrates is insignificant.

These observations led us to suspect that the sputtering of the substrates is due to the formation of negative gold ions at the target surface. These ions are accelerated away from the target by the electric field across the dark space with enough energy to sputter the substrates and prevent film accumulation. Further sputtering experiments and SIMS analysis have confirmed that certain materials have a surprisingly large yield of negative ions under argon ion bombardment. This negative ion flux may affect the accumulation rate, composition, and other properties of the growing film.

Experimental technique

The sputtering experiments were carried out in an rf diode system that has been described elsewhere [3]. Targets were prepared by arc melting followed by melting into a Mo backing plate. A CsAu target was prepared by heating Au foil in Cs vapor in a sealed quartz ampoule for six hours at 450°C (723 K). A sintered target of LaF_3 was also used. Substrates were held on a water-cooled anode with a thermally conducting compound. Target voltages of 500 V to 2500 V were used with an anode voltage (substrate bias) of 50 V.

Measurements of substrate etch rates using the SmAu target were made as a function of substrate material, target voltage, substrate bias voltage, sputtering gas (Ar, Kr, Ne, and He) and pressure. Further studies were made with other compositions in the SmAu system, and with LaAu, NdAu, EuAu, GdAu, TbAu, DyAu, YbAu, YAu, SmCu, SmAg, SmPt, CsAu, and LaF_3.

To correlate negative ion formation with the etching phenomenon, SIMS measurements were carried out on several of the above compounds, using a Cameca ion microscope with a 10 kV argon ion beam. The target is biased to 4.5 kV for ion collection; thus, for negative ion detection the effective accelerating voltage is 14.5 kV and for positive ion detection 5.5 kV. These accelerating energies are higher than the 500-2500 V energies used in the sputtering experiments. We believe that a valid comparison of the negative ion yield of different materials may be made even though the absolute magnitude of negative ion yield is expected to depend on the positive ion accelerating energy.

Experimental results

In this section a summary of experimental results is presented, which illustrates the negative ion behavior. A more complete presentation of the results will be given elsewhere [4].

Sputtering

SmAu binary system

The highest substrate etch rates were measured using a SmAu 1 : 1 composition target. Up to 7 μm of Si is etched in one hour under conditions that would normally deposit 2 to 3 μm of film on the Si substrate. Lower etch rates are found with a target of composition $Sm_{0.75}Au_{0.25}$, and no etching occurs with a $Sm_{0.25}Au_{0.75}$ target.

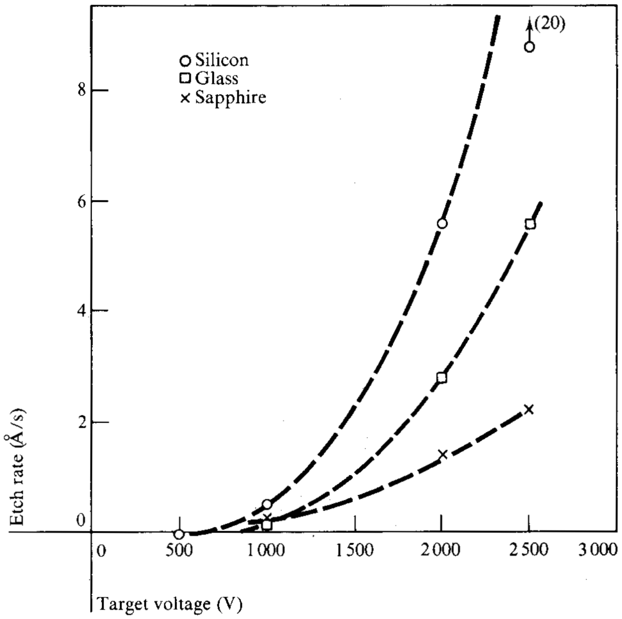


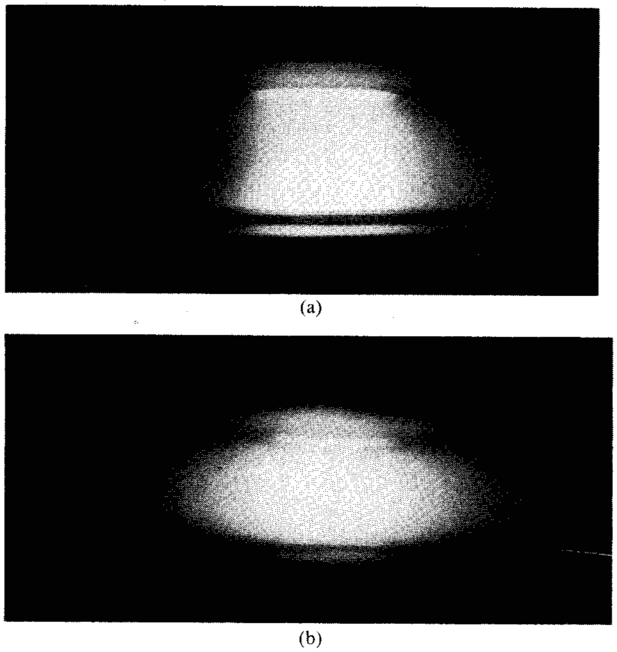
Figure 2 Substrate etch rate vs target voltage for silicon, glass, and sapphire substrates. SmAu target, argon pressure = 4 Pa, V_{bias} = 50 V, target-to-substrate distance = 5 cm.

The most pronounced dependence of substrate etch rate on sputtering parameters is on the target voltage V_t. Figure 2 shows the etch rate of Si, glass and sapphire substrates for target voltages from 500 V to 3000 V (SmAu target, Ar pressure = 4 Pa, V_{bias}(applied) = 50 V, target-to-substrate distance = 5 cm). The dependence of etch rate on substrate material is consistent with the sputter yields of the substrates. The strong dependence on V_t is faster than linear and suggests that the etch rate depends on both the energy and the flux of negative ions from the target. Also, because gold is about five times as heavy as argon, it will have a higher sputtering yield than argon. At low target voltage (below about 750 V for the conditions given above) the substrates are no longer etched, and film deposition occurs, as shown in Fig. 2, by a negative etch rate.

The dependence of etch rate on other sputtering parameters is less pronounced. Etch rate increases with bias voltage and pressure, and preliminary experiments show a lower etch rate when a sputtering gas other than argon is used.

Other Au compounds

To study the range of occurrence of the etching phenomenon, other gold alloys of 1 : 1 composition were investigated. Compounds that show the etching phenomenon



(a)

(b)

Figure 3 Photographs of sputtering glow. (a) CsAu target, showing collimated region under target. (b) DyAu target, showing normal diffuse glow.

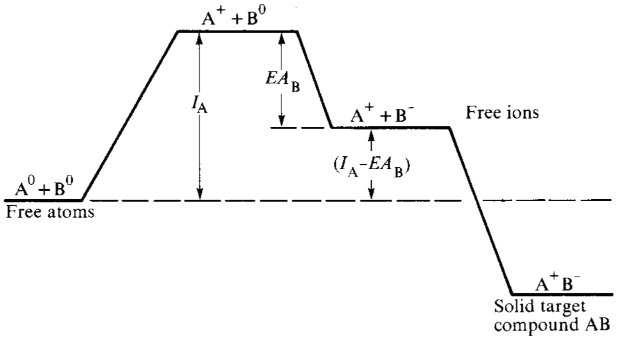


Figure 4 Energy levels involved in electron transfer from element A to element B in the formation of the target compound AB. I_A = ionization potential of element A. EA_B = electron affinity of element B.

include EuAu, LaAu, and CsAu. Those that deposit films include NdAu, GdAu, TbAu, DyAu, YbAu, and YAu. The pattern of occurrence of the etching phenomenon suggested electronegativity as an important parameter, which led to the model discussed here. In the case of CsAu, the glow discharge showed clear evidence of a collimated area between target and substrate [Fig. 3(a)], contrasted with the more diffuse appearance of the DyAu discharge, which deposits normal films [Fig. 3(b)]. Other compounds, however, did not show this distinct effect on the glow. This observation suggests that a more quantitative measurement of the optical spectrum of the plasma may show distinctive features associated with negative ion formation.

Other Sm compounds
Variations of the second constituent were also made. SmAg, SmCu, and SmPt were found to deposit normal films.

- *Secondary Ion Mass Spectrometry (SIMS)*

Examination of several target compounds by SIMS confirmed the generation of large amounts of negative gold ions from target materials that show the etching phenomenon, and small amounts from those materials that deposited normal films. The flux of negative gold ions from SmAu is more than an order of magnitude higher than that from GdAu, which does not show the etching behavior, and several orders of magnitude higher than that from pure Au. Also, the flux of positive gold ions from SmAu is barely detectable, much less than that from pure Au.

Discussion

We have attempted to develop a model that predicts the compounds that will show negative ion production, and those that will not. Because Au has the highest electronegativity of any metal, this was expected to be a controlling parameter. Although the detailed mechanism of how a sputtered Au atom leaves the suface with an attached electron is not yet understood, it seems reasonable that the process will be enhanced when the Au is combined with an element of low electronegativity, which would facilitate electron transfer from that element to the Au. Using electronegativity data recently compiled by Michaelson [5], a tabulation has been made of the electronegativity difference between the constituents of the targets. It has been found that target compounds that show the etching phenomenon have a value of electronegativity difference higher than a certain value, while compounds that do not show etching have a lower value. Only one exception to this pattern, NdAu, was found. Thus it appears that a threshold in electronegativity difference, or ionicity, is probably involved in determining the production of negative ions.

Further consideration of the process of charge transfer suggested treating the target compound more like an ionic solid, even though the ionicity of these metal compounds is not considered to be high. In this way some measure of the energy required to transfer an electron from the first constituent element of the target compound AB to the second element may be obtained. Figure 4 show the conceptual steps involved. Starting from isolated neutral atoms A and B, an energy equal to the ionization potential I_A must be supplied to remove an electron from A, giving A^+. An energy equal to the electron affinity of element B, EA_B, is gained back by forming a negative ion B^-. Thus the difference $(I_A - EA_B)$ is a measure of the difficulty of transferring an electron from A to B. In the solid the energy is lower (final level in Fig. 4) due to the Coulomb attraction and formation of bands in the metal. A tabulation of $(I_A - EA_B)$ from Refs. [2] and [6] was made and is shown in Table 1 for some of the compounds studied. Here again a threshold value (about 3.4 eV) is found above which the compounds deposit normal films and below which etching of substrates is observed. Again, NdAu is an exception.

The tabulation of $(I_A - EA_B)$ is felt to be more applicable than the difference of electronegativity because electronegativity is the average of I and EA for the same element, and therefore weighs the situation of donor and acceptor equally.

Negative ion production may not necessarily result in substrate etching in the sputtering configuration. For example, neutral flux from the target may mask the negative ion bombardment and result in depositing a film. This appears to be the case for $Sm_{0.25}Au_{0.75}$, which shows a negative gold ion yield in SIMS but deposits a film. It is felt that detailed SIMS measurements will show that negative ion production is not characterized by a sharp threshold, but occurs over a wide range of target compositions to varying degrees. Negative ion yield analysis may also be a useful tool in studying charge transfer in compounds.

By using the threshold value of 3.4 eV, other target compounds may be predicted to show the etching phenomenon, at least under conditions similar to those used here. We predict that most fluorides, chlorides and bromides will exhibit etching by negative ions (chemical etching may also occur in these cases), as will several carbides, oxides, sulfides and gold compounds. Also, many compounds with the alkali metals Li, Na, K, Rb, and Cs will exhibit negative ions of the second element. We believe that various anomalous results in the sputtering of oxides and nitrides, such as suppressed deposition rates or changes in stoichiometry, may be related to negative ion formation. It may also be possible to influence the degree of negative ion formation through changes in sputtering parameters and thereby gain control over effects on thin film deposition processes. Direct use of the negative ion flux for the etching of substrates may have important differences from the usual sputter-etching process, in which the substrates are placed on the cathode.

Conclusions

The sputtering of certain compounds has been found to generate large quantities of negative ions, which are capable of modifying film properties and suppressing deposition rates to the point of substrate etching. SIMS analysis confirms large yields of negative ions from these compounds. A model based on ionization potential and electron affinity predicts the occurrence of negative ions and correlates with the observed etching phenomenon. The model predicts that negative ion phenomena will occur in a wider range of materials than expected. Quantitative SIMS analysis must also take account of negative ion yields.

Table 1 Tabulation of data indicating alloy constituents that will cause etching during the sputtering process.[a]

Compound AB	I_A (eV)	EA_B (eV)	$(I_A\text{-}EA_B)$ (eV)	*Etch*	*Deposit*
CsAu	3.89	2.31	1.58	x	
LaF_3	5.58	3.40	2.18	x	
NdAu	5.49	2.31	3.18		x
LaAu	5.58	2.31	3.27	x	
SmAu	5.63	2.31	3.32	x	
EuAu	5.67	2.31	3.36	x	
SmPt	5.63	2.13	3.50		x
TbAu	5.85	2.31	3.54		x
DyAu	5.93	2.31	3.62		x
GdAu	6.14	2.31	3.83		x
YbAu	6.25	2.31	3.94		x
YAu	6.38	2.31	4.07		x
SmAg	5.63	1.30	4.33		x
SmCu	5.63	1.23	4.40		x

[a] Values of I from Ref. [6] and EA from Ref. [2].

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References

1. J. J. Hanak and J. P. Pellicane, "Effect of Secondary Electrons and Negative Ions on Sputtering of Films," *J. Vac. Sci. Technol.* **13,** 406 (1976).
2. H. Hotop and W. C. Lineberger, "Binding Energies in Atomic Negative Ions," *J. Phys. Chem. Ref. Data* **4,** 539 (1975).
3. J. J. Cuomo and R. J. Gambino, "Influence of Sputtering Parameters on the Composition of Multi-component Films," *J. Vac. Sci. Technol.* **12,** 79 (1975).
4. J. J. Cuomo, R. J. Gambino, J. M. E. Harper, J. D. Kuptsis, and J. C. Webber, submitted to American Vacuum Society.
5. H. B. Michaelson, "Relation Between an Atomic Electronegativity Scale and the Work Function," *IBM J. Res. Develop.*, to be published in January 1978.
6. C. E. Moore, *National Standard Reference Data Series* **34,** U.S. Government Printing Office, Washington, D.C., 1970.

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