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Matrix Effects in Ion-Induced Auger Emission as Observed in Ne Collisions With Cu-Mg and Cu-Al Alloys

John Ferrante and Stephen V. Pepper
Lewis Research Center
Cleveland, Ohio

September 1983

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ABA:  Author
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MATRIX EFFECTS IN ION-INDUCED AUGER EMISSION AS OBSERVED IN Ne COLLISIONS WITH Cu-Mg AND Cu-Al ALLOYS

John Ferrante and Stephen V. Pepper
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

E-1532

SUMMARY

Ion-induced Auger electron emission is used to study the surfaces of Al, Mg, Cu - 10 at.% Al, Cu - 19.6 at.% Al, and Cu - 7.4 at.% Mg. A neon (Ne) ion beam whose energy is varied from 0.5 to 3 keV is directed at the surface. Excitation of the lighter Ne occurs by the promotion mechanism of Barat and Lichten in asymmetric collisons with Al or Mg atoms. Two principal Auger peaks are observed in the Ne spectrum: one at 22 eV and one at 25 eV. Strong matrix effects are observed in the alloys as a function of energy in which the population of the second peak is greatly enhanced relative to the first over the pure materials. For the pure material over this energy range this ratio is <1.0. For the alloys it can rise to 4.0. Thus, an interesting effect is observed which may be of relevance to the electronic structure of alloys and to other surface tools such as secondary ion mass spectroscopy.

INTRODUCTION

The topic of Auger emission from solids resulting from ion bombardment (refs. 1 to 3) has received little interest among surface scientists. Its primary use has been in ion beam alignment and quantitative SIMS. Although it has been suggested that it may be useful in detecting rare gas implantation (ref. 2) or surface composition in certain alloys (refs. 4 to 6), there is a good reason for this lack of interest. The Auger spectrum from the surface is very atomic like. That is, the deexcitation process appears in sputtered particles and is thus decoupled from the substrate.

In recent papers (refs. 7 and 8) the authors reported a study of the bombardment of solid Mg, Al, and Si surfaces by Ne ions with incident energies from 0.5 to 3 keV. In this study Auger electrons from the projectile as well as from the substrate were observed. This occurs since the promotion mechanism of Barat and Lichten (ref. 9) favors excitation of the lighter atom. Thus an asymmetrical collision between Ne and the substrate atom produced the excitation. The substrate excitations were produced by the symmetrical knock on collisions between substrate atoms.

The authors observed two principal peaks in the Auger spectrum of the deexciting Ne at 21.9 and 25.1 eV. In pure materials the peak at 25 eV was substantially larger than that at 22 eV. The authors report in reference 8 that in alloys of these materials the relative magnitude of these two peaks inverts and thus there is a matrix effect indicating that the substrate is affecting the ion-induced Auger emission process. Hiraki, et al. (ref. 5) and Iwani, et al. (ref. 6), also report an alloy effect in Si alloys. In their case there were also two Auger peaks of interest - one described as atomic like and the other as bulk like. They found an enhancement of the atomic like peak in the alloys presumably as a result of a change of species as nearest neighbors.

In this paper we report the relative population of the 25 and 22 eV Ne peaks as a function of bombardment energy and angle of incidence for pure Mg and Al and Cu-Al and Cu-Mg alloys.

EXPERIMENTAL

The experiments were performed in a standard ultrahigh vacuum system with a base pressure of 1×10^{-10} torr. The ion gun used was equipment commercially available for sputter cleaning surfaces and depth profiling with a nominal spot size of 2 mm. Both retarding field analyzers and cylindrical mirror analyzers were used for Auger analysis.

The experiment was performed by turning off the ion pumps and backfilling the system to 5×10^{-5} torr Ne. The surfaces were sputter cleaned until no oxygen or carbon were seen in the electron induced Auger spectrum. The electron gun was then turned off leaving the ion-induced AES spectrum. The angle of incidence (angle between the ion beam and the surface normal) was varied between 5° and 85°. At each angle the beam energy was varied from 0.5 to 3 keV. The ion-induced Auger spectrum was taken at each setting. Auger spectra were taken with a 2-V p-p modulation voltage. The samples used were pure Mg, pure Al, Cu - 7.4 at.% Mg, Cu - 10 at.% Al and Cu - 10.6 at.% Al. Some typical spectrum results for pure Mg and Cu-Mg and Cu-Al alloys are shown in figure 1. As can readily be seen, the population of the second Ne state is greatly enhanced over the first in the alloys. It is interesting to examine the energy dependence at a fixed energy. The ratio is used since it is difficult to determine geometrical effects such as acceptance angles at the CMA as the angle is varied; also, the ion beam current is a function of energy. Hopefully these effects are cancelled by using the ratio. We will use the nomenclature R for the ratio where

$$R = \frac{\text{Peak to peak height of 25 eV feature}}{\text{Peak to peak height of 22 eV feature}}$$

Actually, an indication of a material effect was previously reported by the authors in reference 8. We can see that there is a substantial variation in this ratio depending on material with R_{Mg}, R_{Al}, and R_{Si} (fig. 2).

In figure 3 we show the energy dependence of R for the pure materials and the Cu-Mg and Cu-Al alloys. We see that R increases with energy for both pure materials and the alloys. However, with the alloys we have a very strong energy dependence; in fact, there is inversion of population of the Ne excited states which produces the final state. We also see that unlike the pure materials the energy dependence in the Cu-Mg alloy is very strong since there is only 7 at.% Mg in this alloy whereas we have 20 at.% Al in the other. The Cu-Mg alloys are above the solubility limit (ref. 10) and are probably a mixture of intermetallics and solid solutions. The Cu - 19.6 at.% Al is at the solubility limit and is also probably a mixture. The Cu - 10 at.% Al is a single crystal solid solution.

Figure 4 shows the angular dependence for pure Al and Cu - 19.6 at. % Al for two incident energies (1000 and 2500 eV). These represent the trends observed in all cases. There seems to be a strange dependence in that there seems to be an increase in R for both more normal and grazing incidence. The trends in the pure materials and the alloys are the same.

DISCUSSION

The authors reported in references 7 and 8 on ion-induced Auger electron emission from Ne interactions with Mg, Al, and Si surfaces. In those papers a material dependence was reported for the population of the two principal Ne Auger peaks at 22 and 25 eV. In this paper those results are expanded, and the material dependence in alloys is investigated in more detail. The most important result of this study is the strong energy dependence (fig. 3) and the population inversion of the two peaks as compared with collisions with the pure materials. This result indicates that work must be done in determining physical models for the collision and excitation process. Zampieri and Baragiola (ref. 11) have proposed an explanation for the excited states that produce the observed peaks based on the work of Anderson, Olsen, and Bisgaard (refs. 12 to 14) which differs from that of the authors. They speculate that the transitions arise from excited states that involve two holes in the 2p level of Ne - e.g., $2p^4\ 3s^2$ states rather than a 2s hole. This identification is probably correct because the bombardment energies are sufficiently low that the distance of closest approach needed to obtain a 2s hole is not achieved and adiabatic (ref. 9) effects dominate. This excitation scheme leads to 18 possible transitions out of which only three are observed - two principle peaks and one much weaker at 27 eV. Zampieri and Baragiola argue that if the binding energy of the excited states is less than the work function that resonance ionization of the Ne occurs by tunneling into empty states in the conduction band. This would eliminate all but six of the states. They further argue that three of the remaining six that have binding energies greater than but close to the work function have their binding energies shifted to lower values by interaction of the Ne with the metal. Finally, they argue not unreasonably that the population of the two states which they identify as giving the two Ne peaks [$2p^4\ (^3p)\ 3s^2\ ^3p$, $2p^4\ (^1D)\ 3s^2\ ^1D$] should be in the ratio of their multiplicities, 9:5. Unfortunately, these results do not fit the previous and present observations of the authors.

First, the arguments concerning eliminating certain transition based on the work function of Al must be reconsidered since the same peaks are observed for three materials (Mg, Al, and Si); e.g., the work function of Al is 4.2 eV whereas that of Mg is 3.7 eV (ref. 15). If we examine figure 2 we see that $R_{Mg} << 1$ whereas $R_{Si} \approx 1$. Also, in the present work we show that there is an energy dependence for R even with pure materials (fig. 3) R (3000 eV) > R (500 eV). Finally, we see that there is a strong energy dependence in the alloys leading to a inversion of population of the states producing the Auger peaks. The angular dependence of R (fig. 4) unfortunately provides no additional information since the trends are the same for both pure materials and alloys.

Thus, we have a very interesting matrix effect in ion-induced Auger emission which requires detailed knowledge of the collision kinematics as well as the electronic processes involved in creating the excited states. It is possible that understanding these processes could lead to a new diagnostic tool for certain alloys.

Finally, we would like to comment on a controversy over the interpretation of the principal Ne peaks that has appeared in the literature (refs. 8, 10, and 16). The present authors assert that the origin of the Ne peaks is due to asymmetric collisions between the Ne and substrate atoms. The primary reasons for this assertion are no dose dependence with implanted Ne, the lack of ion-induced peaks in other materials highly dosed with Ne, and the correct sensitivity dependence according to the promotion mechanism for Mg, Al, and Si. Benezeth, et al. (ref. 16), state that the peaks are due to symmetric collisions with implanted Ne. They argue that the low energy for the maximum in the collision cross section and a lack of a Doppler shift in the spectrum of the recoiling Ne as detected by them are evidence for symmetric collisions. Zampieri and Baragiola (ref. 11) have detected the Doppler shift in the recoiling Ne spectra. There remains the low energy for the maximum in the production cross section. A low energy maximum in the cross section might be expected in asymmetric collisions which are probably a surface process, since at higher energies there will be greater penetration of the Ne and thus the escape of the emitted low energy electrons would be more difficult. However, if this is not a strong factor we have the population increase of the second feature (25 eV) indicating that as the incident energy is increased the population of the first peak may decrease whereas the second may continue to increase. It is evident that further studies are needed.

CONCLUSION

Strong matrix effects are observed in the spectrum of ion-induced Auger peaks for Ne in collision with certain materials. These matrix effects are manifested by population inversion with energy of the two Ne Auger peaks at 22 and 25 eV in Cu-Mg and Cu-Al alloys. It is possible that this effect may provide information concerning the electronic structure of alloys. Further study is needed to investigate the implication of these observations.

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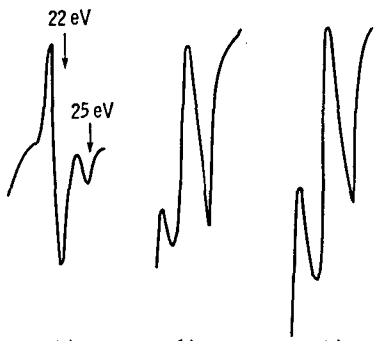

(a) (b) (c)

(a) Pure Mg.

(b) Cu - 7.4 at. % Mg alloy.

(c) Cu - 19.6 at. % Al alloy.

Figure 1. - Typical ion-induced Ne Auger peak taken at V_B = 3000 V and an angle of 60° with surface normal.

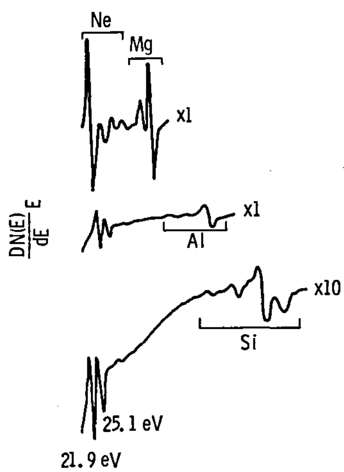

Figure 2. - Auger spectra from Si, Al, and Mg bombarded by 3 keV Ne^+. E_{mod} = 0.75 eV p-p, angle of incidence = 60° from surface normal. (Spectrum from Si amplified by 10 relative to the spectra from Al and Mg.)

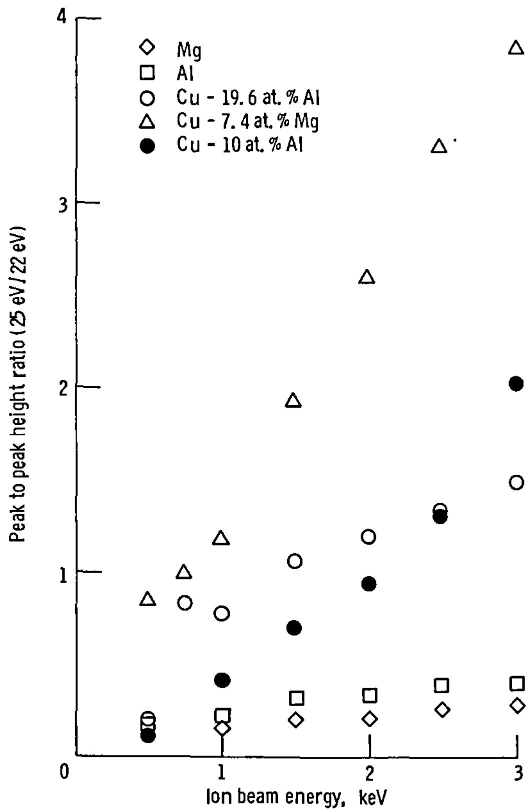

Figure 3. - Ratio of 25 to 22 eV Ne peak to peak heights as function of incident ion energy for ion beam at 30° with the surface normal.

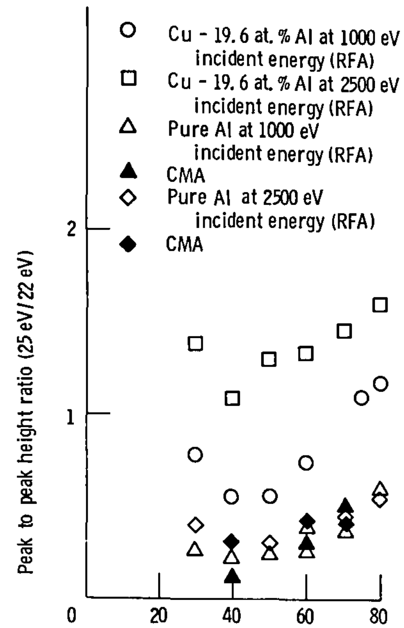

Figure 4. - Neon peak height ratio (25 eV/22 eV) as function of angle at incidence (angle between ion beam and surface normal).

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