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# Sputtering of neutral clusters from silver–gold alloys

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ABSTRACT

Polycrystalline Ag, $Ag_{20}Au_{80}$, $Ag_{40}Au_{60}$, $Ag_{80}Au_{20}$ and Au samples were bombarded with 15 keV $Ar^+$ at 60° incidence and the resulting secondary neutral yield distribution was studied by non-resonant laser postionisation mass spectrometry. Neutral clusters containing up to 21 atoms were observed for the targets. The yield of neutral clusters, $Ag_mAu_{n-m}$, containing $n$ atoms, $Y_n$, was found to follow a power in $n$, i.e. $Y_n \propto n^{-\delta}$, where the exponent δ varied from 3.2 to 4.0. For a fixed $n$, the cluster yields showed a variation with number of gold atoms similar to that expected for a binomial distribution. In addition, the cluster compositions from the sputtered alloys were indicative of sputtering from a gold rich surface.


## 1. Introduction

It is well known that the sputter yield, $Y_n$, of neutral clusters of $n$ atoms sputtered from a range of elements is given by a power law

$$Y_n \sim n^{-\delta} \quad (1)$$

where $\delta$ was found to be monotonically related to the total sputter yield [1]. This observation means that elements with higher sputter yields were more likely to eject high mass clusters and so have a lower value of $\delta$. This power law relationship has also been found from molecular dynamics simulations of sputtering [2] and related to ejection of neighbouring near-surface atoms due to upward energy transfer from deeper layers within the target [3]. Although many measurements of yields of different sized clusters have been made for sputtered elemental targets, there have been very few measurements made for neutral clusters sputtered from alloy targets. Since sputtering is a common method for thin film fabrication, a knowledge of the composition of sputtered clusters is a first step for understanding the deposition process, especially for nanoparticle formation in the vapour phase and on surfaces.

Since alloy sputter yields generally lie between the sputter yields of the constituent elements [4], we may expect that values of $\delta$ for sputtered mixed neutral clusters from alloys should lie between the values of $\delta$ for the individual elemental clusters. However, the distribution of mixed neutral clusters sputtered from NiAl [5] and CuAu [6] alloys gave values of $\delta$ lower and higher, respectively than that for clusters sputtered from the individual pure elements. This difference for NiAl was attributed to the greater stability of the mixed clusters arising from the greater Ni–Al bond strength compared to Al–Al or Ni–Ni, making the sputtering of such clusters more likely. Since the Cu–Au (179 kJ $mol^{-1}$) bond strength is similar to that of Cu–Cu (168 kJ $mol^{-1}$) or Au–Au (184 kJ $mol^{-1}$), the additional stability of the mixed clusters would not be so pronounced and so less mixed sputtered clusters would be expected. In addition, the difference in mass between Cu and Au would lead to less efficient energy transfer during collisions leading to sputtering so that less mixed clusters would be produced. In this paper, we will test the mass effect by measuring the yields of elemental and mixed clusters ejected from Au and Ag which have similar bond strength differences to Cu and Au but masses which do not differ as much as Cu and Au.

## 2. Experimental

Measurements of the sputtered neutral clusters flux were made on an instrument that has been described previously [7] and using a procedure also described previously [6]. NIST standard reference materials (SRM482) were used for the Ag, Au and 4 alloy samples ($Ag_{20}Au_{80}$, $Ag_{40}Au_{60}$, $Ag_{60}Au_{40}$, $Ag_{80}Au_{20}$). The samples were sputtered with 15 keV $Ar^+$ beam incident at 60° until an equilibrium surface concentration. The ion beam was then pulsed for time of flight (TOF) measurements. For a given mass spectrum,

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the primary ion beam was turned on for 2 μs in order to fill a volume with sputtered neutrals extending 3 mm from the surface plane. The ion beam was then stopped, and secondary ions were swept out of the plume with a high voltage pulse. In a time 800 ns following the end of the rejection pulse, a $F_2$ laser (GAM 100EXF) with a wavelength of 157 nm was fired and its beam passed through the plume. This delay was chosen to maximize the overall cluster yield. The atoms in the plume were photoionised and extracted into a TOF mass spectrometer. The $F_2$ laser beam was transported to the analysis chamber in an ultrahigh vacuum. Up to three neutral density filters (0.5, 1.0 and 2.0 OD) could be independently placed in the path of the laser beam to allow for 5 levels of beam attenuation over 2 decades of intensity. The filter accuracy and linearity had been previously confirmed by performing a power study on sputtered indium atoms. Two $MgF_2$ lenses were also placed in the beam path to provide fine adjustment of the beam passing over the target. A beam rotator was used to change the vertical focus of the GAM laser output to a horizontal beam focus parallel to and a fraction of a millimeter above the horizontally mounted sample surface. For laser energies of 0.5 mJ in a 10 ns pulse, laser peak power densities ranging from $10^5$ to $10^7$ W/cm$^2$ were achieved. The photoions formed by the laser were accelerated into a 1.2 m long reflectron TOF mass analyzer and detected using a Burle bipolar detector.

## 3. Results and discussion

Fig. 1 shows that the measured spectrum of clusters desorbed from $Ag_{60}Au_{40}$ extends to masses greater than 5000 amu. The inset in Fig. 1 shows that clusters have compositions in the sequence $Au_{m-n}Ag_{2n}$ or $Au_{m-n}Ag_{2n+1}$ ($n = 0, 1, 2, \ldots$) and can be easily distinguished. Although clusters containing more than 30 atoms are observed, the detailed analysis of individual cluster yields has not then been taken beyond 21 atom clusters due to decreasing signal to background ratios.

The integrals of the individual peaks in the mass spectrum for selected clusters sputtered from $Ag_{40}Au_{60}$ are presented in Fig. 2 as a function of laser intensity. The slopes of all the curves at lower laser intensities, with the exception of Au, are approximately unity. A linear slope is a signature of a single photon ionisation process since, for such a process, the photoion signal, $S$, varies with laser intensity, $P_L$, as [8]

$$S = S_{sat}\left(1 - \exp\left(\frac{-\sigma P_L \Delta t}{h\nu}\right)\right) \quad (2)$$

where $S_{sat}$ is the signal intensity at saturation, $\sigma$ is the photoabsorption cross-section, $h\nu$ is the laser photon energy of

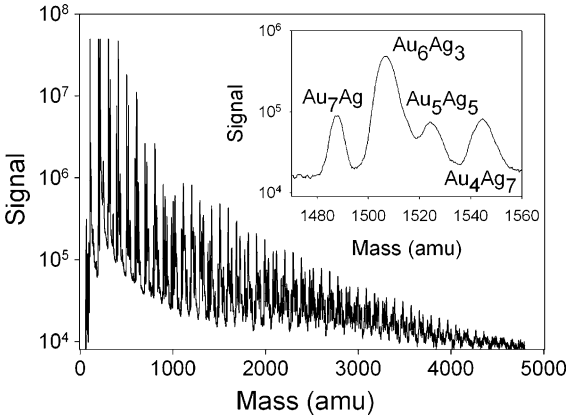


**Fig. 1.** Yield of photoions from clusters sputtered from $Ag_{60}Au_{40}$ by 15 keV $Ar^+$ at 60° incidence. The inset shows detail of the mass spectrum from 1480 to 1560 amu illustrating peaks corresponding to individual clusters.

7.89 eV and $\Delta t$ is the laser pulse width of 10 ns. As Au has an ionisation potential of over 9 eV, the two photon ionisation process expected for this cluster is consistent with the observed slope of approximately 2. It is surprising that all but the most gold rich clusters are ionised with a single photon since the IP for many of the gold rich clusters is above 7.9 eV. For example, calculated values of the vertical IP for $Au_6$, $Au_5Ag$, $Au_4Ag_2$ and $Au_3Ag_3$ are all greater than 8 eV [9]. However, clusters are sputtered in (ro-)vibrationally excited states so that the effective IP of the cluster may be reduced by 0.5 eV or more compared to a cluster in the ground state [2,10]. All clusters reach saturation at the highest laser intensity except for Au and $Au_3$ in Fig. 2 but the signal for some clusters is falling for a laser intensity of $10^7$ W cm$^{-2}$. The photoabsorbtion cross-section is known to rise with cluster size [11] leading to saturation at lower laser intensities for the larger clusters as observed in Fig. 2. At higher laser intensities, fragmentation of clusters during photoionisation may occur due to multiphoton excitation, giving rise to the decrease in intensity observed at $10^7$ W cm$^{-2}$. Therefore the data used in the following discussion was taken at a laser intensity of $3 \times 10^6$ W cm$^{-2}$.

Fig. 3 shows that the relative yields of $Ag_mAu_{n-m}$ clusters sputtered from $Ag_{60}Au_{40}$ varies with both $n$ and $m$. The cluster yield would be expected to be related to the probability of ejecting a cluster containing $n$ Au and Ag atoms times the probability, $P(n, m)$, that the cluster contained $m$ Au atoms. If we assume a binomial distribution for $P(n, m)$ then

$$P(n,m) = \frac{n!x^m(1-x)^{n-m}}{m!(n-m)!} \quad (3)$$

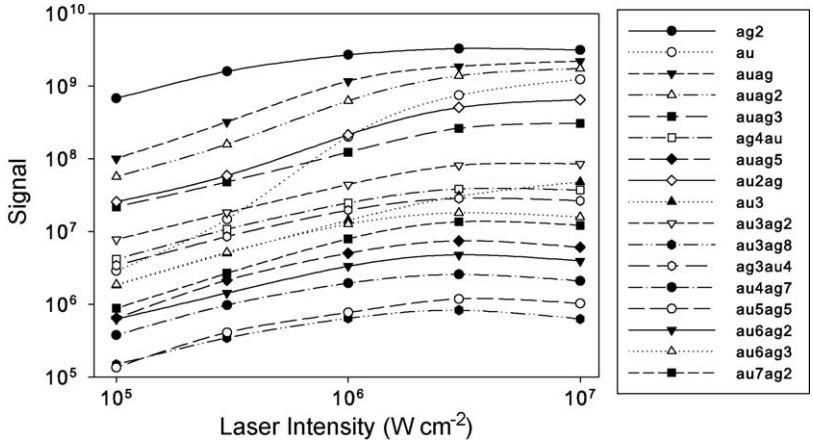


**Fig. 2.** Variation of a selection of cluster signals with laser power sputtered from $Ag_{40}Au_{60}$ irradiated with 15 keV Ar at 60° incidence.