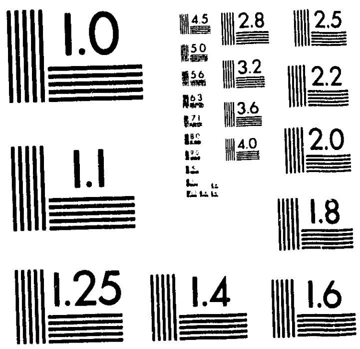
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Neutral Copper Cluster Sputtering Yields: Ne^+, Ar^+ and Xe^+ Bombardment*

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Abstract

The sputtering of neutral metal clusters was investigated by measuring relative sputtering yields of copper clusters ejected from polycrystalline copper under 3.9 keV bombardment by Ne^+, Ar^+ and Xe^+ ions at normal incidence. The yields of clusters from Ne^+ bombardment were lower than those from Ar^+ bombardment, and yields from Ar^+ bombardment were lower than those from Xe^+ bombardment. The sputtering yield ratios Ne^+/Ar^+ and Xe^+/Ar^+ were measured to be 0.56 and 1.08. The size distribution of the sputtered clusters can be fit by a power law dependence with exponents of -8.1, -8.2 and -6.2 for Ne^+, Ar^+ and Xe^+, respectively. The similarity of the exponents of the Ne^+ and Ar^+ power law fits indicates that the sputtering yields for these two primary ions are similar while that for Xe^+ is substantially higher, in contrast to the sputtering yield ratio data. The difference between the two measurements can be explained by assuming a systematic uncertainty in the sputtering yield ratio measurements that makes the measured ratios lower than the true values. Assuming a value at the high end of the experimental Ne^+ sputtering yield range, the exponents of the power law fits exhibit a linear dependence on the total sputtering yield.

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Introduction

The sputtering of metal clusters has been a subject of experimental and theoretical interest for about 35 years. However, for the first 15 years, only the ion fraction of the sputtered flux was detected owing to the difficulties in detecting neutral species. Since secondary ions are much more susceptible than neutrals to the chemical environment at the surface, it was unclear whether these results were generalizable to the total sputtered flux. Some twenty years ago, the first neutral metal clusters were observed [1-3], but the postionization efficiencies were low and only small clusters could be detected. This situation has persisted up until the last few years. With the recent application of laser postionization [4-7], and in particular, single-photon ionization [8-12], to the sputtered flux, a new range of sputtered species has become accessible to experimentation. In recent experiments, sputtered neutral clusters as large as Cu_{20} [8, 10], Al_{12} [10], Ag_{18} [12] and In_{32} [13] have been observed, and kinetic energy distributions for Cu and Al clusters out to 6 atoms [9-11], Ag clusters out to 5 atoms [12], and In clusters out to 9 atoms [14] have been measured. Recently, we observed that the size distributions of sputtered neutral Cu and Al clusters exhibit a power law dependence on the number of atoms in the cluster. This was closely followed by demonstrations of the same phenomenon for Ag [15] and In [13] clusters. We then were able to identify a linear dependence of the power law exponent on total sputtering yield [10]. Changing the bombarding ion is another way to change the total sputtering yield of a system. In this paper, we report measurements of the relative copper cluster sputtering yields from Ne^+, Ar^+ and Xe^+ bombardment of polycrystalline copper.

Experimental

The experiments were performed on the SARISA IV secondary neutral mass spectrometer, which has been described in detail previously [16, 17]. Briefly, a 1 μs pulse of 3.9 keV noble gas ions from the Colutron G1 ion gun is focussed and directed onto the Marz grade polycrystalline copper target at normal incidence. After the end of the ion pulse, the laser is fired into the region above the target surface, photoionizing a portion of the neutral sputtered flux. The photoions are extracted into an energy- and angle-refocussing time-of-flight mass spectrometer and are detected by microchannel plates in a chevron arrangement. The output from the detector is either digitized directly or pulse counted, depending on the signal level.

The procedure for measuring neutral copper cluster yields has been described previously [8, 10]. The neutrals were photoionized by the 6.4 eV photons from an ArF excimer laser (power density = $10^4 - 10^5$ W/cm^2). Cu, Cu_2, Cu_4 and Cu_6 must absorb two photons to exceed the ionization potential, while Cu_3, Cu_5 and clusters larger than Cu_6 are one-photon ionizable. In order to normalize the cluster yields to the sputtering yield of the atom for each primary ion, the atoms were resonantly ionized by a two-color two-photon ionization scheme employing the 327.4 nm transition from the $^2S_{1/2}$ ground state to the $^2P_{3/2}$ state for the first step and 193 nm (ArF) for the ionization step. Since the ionization step was not saturated, the power dependence of the atom signal on the ArF laser power density, I, was measured. The experimentally determined power dependence was $I^{1.35}$. The exponent is larger than the expected value of 1 because of volume effects in the photoionization region.

To measure the relative neutral cluster sputtering yields for different primary ions, mass spectra of the sputtered flux were first taken with Ar^+ sputtering. Since larger clusters have lower velocities [9, 10], the laser delay time was varied to optimize the signal for each cluster. The atom signal using resonant ionization, the primary ion current, and the ArF laser power were also recorded. Then the Ar gas was pumped out of the ion gun, and either Ne or Xe was installed as the primary ion. The various voltages and deflection timings in the ion gun were adjusted to create a 1 μs pulse of the new primary ion. A Faraday cup was used to insure that the ion beam always struck the center of the target. Mass spectra of the sputtered flux using the new primary ion were then taken, again optimizing laser timing for signal and recording the resonant atom signal, the ion current, and the laser power. Typical ion currents to the target were 2 μA for Ar^+ and Ne^+ and 0.75 μA for Xe^+.

To quantify the relative yields of the clusters sputtered by the different primary ions, the resonantly ionized atom signal was assumed to be proportional to the total sputtering yield, to the primary ion current, to $I^{1.35}$, and to the transmission of the instrument. Using resonant ionization was important, since we have determined that the atomic ion signal from two-photon nonresonant ArF ionization at this power density is solely from photofragmentation of dimers to atomic ions [18]. Thus the nonresonant atom signal (from dimers) would not be expected to be proportional to the sputtering yield. The resonant atom signals for the different primary ions were corrected for the primary ion current and the laser power density. The resultant signals are proportional to the sputtering yield and to the instrument transmission. Since we have no way of independently measuring the instrument transmission when the primary ion is changed, changes in this transmission are a source of uncertainty in our measurements. The cluster intensities were scaled with the atom signal and were also corrected for changes in laser power (assuming a linear power dependence) and ion current during the experiment. The laser power typically dropped about 20% over the course of the measurement on one primary ion. The ion current remained essentially constant in all experiments except for the Ne^+ bombardment, in which it dropped 35%. In addition, the transmission of the instrument was lower by 15–20% at the end of each Ar^+ bombardment than at the beginning of the experiment. Less than 10% change in transmission was observed during the course of the Ne^+ and Xe^+ bombardments. Each cluster signal also needs to be corrected for the average velocity of the cluster. Since the signal in the experiment is proportional to the density of a species in the ionization region, the signal for each cluster must be multiplied by the average velocity to convert to flux. Recent measurements indicate that the energy distributions of sputtered neutral clusters are similar [8-12], and thus, the average velocity can be approximated by $n^{-0.5}$, where n is the number of atoms in the cluster.

Results and Discussion

The relative intensities of neutral copper clusters obtained from the procedure described above are shown in fig. 1. The atom signal from Ar^+ sputtering has been set equal to 1 since this experiment can determine on relative sputtering yields. The atom points for Ne^+ and Xe^+ bombardment are therefore the experimental measurement of the sputtering yield ratio to Ar^+ for those primary ions. The sputtering yield data for polycrystalline copper bombarded by 3.9 keV Ne^+ indicates that the actual sputtering yield is somewhere in the range 2.5 – 4.5 atoms/ion. The sputtering yields for Ar^+ and Xe^+ bombardment are reported to be 5 and 8 atoms/ion, respectively [19, 20]. Our Ne^+/Ar^+ experimental value is 0.56, which would indicate a sputtering yield for Ne^+ bombardment at the low end of the experimental range. However, the experimental Xe^+/Ar^+ ratio is 1.08, approximately 30% lower than the expected value of 1.6. As will be discussed below, there is evidence for a systematic error which would make both of the experimental yield ratios too low.

The relative intensities of the neutral copper clusters were measured out to Cu_{14} for Ne^+ and Ar^+ sputtering and out to Cu_{17} for Xe^+ sputtering. Not surprisingly, cluster yields from Ne^+ sputtering are lower than from Ar^+ sputtering, and these in turn are lower than those from Xe^+ sputtering. It is obvious from the figure that the sputtering yields of large clusters are much more affected by the change from Ar^+ to Xe^+ than the yields of small clusters. It should be emphasized that within a primary ion data set, the points represent relative intensities and *not* lower limits of the sputtering yields, as we have measured in the past [8, 10]. In the current experiments, the atom ionization was not saturated. While the resonantly ionized atom signal provides a means of measuring the sputtering yield from one primary ion relative to another, it provides no absolute measurement to scale the cluster yields to because of the lack of saturation. To illustrate the point, the saturated atom signal is estimated to be approximately two orders of magnitude above the atom signals observed in these experiments. It is expected, however, that the one-photon-ionized species will have similar ionization efficiencies, and so their relative intensities are assumed to represent relative abundances.

The size distribution for bombardment with all three primary ions shows a general decrease with increasing cluster size. The points for Cu_2, Cu_4 and Cu_6 are artificially low because of the lower ionization efficiency for these two-photon ionized species. Disregarding the points for these clusters and for the atom, it is seen that the size distributions follow power law dependences, as first demonstrated in ref. [10] for sputtering of Cu and Al and also recently in refs. [15] and [13] for sputtering of Ag and In, respectively. The power law fits to the data are shown in fig. 2. The exponent of the power law dependence for Ne^+ sputtering is the same as that for Ar^+ sputtering within the experimental uncertainty. The exponent of the fit for Xe^+ sputtering is much less negative than the other two exponents.

We have recently reported a linear dependence of the power law exponent on total sputtering yield, which was observed for Ar^+ sputtering of four different metal targets [10]. That data is shown in fig. 3, along with the data from this work. The dotted squares are the exponents of power law fits to cluster size distributions from Ar^+ sputtering of Al, Cu, Ag, and In. The filled circles are the exponents obtained in this work. The exponent for Ar^+ sputtering measured here is in reasonable agreement with our previous measurement of -7.8 [10]. The exponent of the Xe^+ size distribution fit is in good agreement with the linear relationship. However, a value for the Ne^+ sputtering yield at the low end of the experimental range, which is indicated by the measured Ne^+/Ar^+ sputtering yield ratio of 0.56, would put the Ne^+ data point far away from the linear dependence. The Ne^+ sputtering data point agrees best with the linear dependence if the sputtering yield is assumed to lie at the high end of the experimental range of data. Thus, the sputtering yield ratios and the size distribution measurements give conflicting results about the relative sputtering yields of copper bombarded by Ne^+, Ar^+, and Xe^+ ions. The measured sputtering yield ratios indicate that Ne^+ and Ar^+ bombardment give different sputtering yields, but that Ar^+ and Xe^+ bombardment give almost the same sputtering yields. The fits of the size distributions to a power law indicate that Ne^+ and Ar^+ give similar sputtering yields, but that Xe^+ gives a higher sputtering yield.

Analysis of the experimental procedure may help to explain why our experimental determination of the sputtering yield ratios appears to be too low. In measuring the sputtering yield ratios, we always started with Ar^+ sputtering and changed to another primary ion later. Since the instrument was optimized at the beginning of the day on Ar^+, any deterioration in the instrument transmission would result in an artificially low sputtering yield measurement for the second primary ion. Therefore, the Ne^+/Ar^+ and Xe^+/Ar^+ ratios that we measure are likely to be lower than the true ratios. This suggests that the Ne^+ sputtering yield could be similar to that of Ar^+, as the exponents of the power law fits to the size distribution indicate. In addition, this reasoning explains why the measured Xe^+/Ar^+ ratio is so close to 1, even though the exponents of the size distribution power laws are different. Taking a closer look at the sputtering yield data in the literature [19, 20], we note that a suitable curve drawn through the most recent data [21, 22] predicts a sputtering yield for Ne^+ bombardment of 4 – 4.5 atoms/ion. Therefore, it seems likely that the sputtering yield of copper under Ne^+ bombardment could indeed be quite close to the yield under Ar^+ bombardment. Assuming that the value for the Ne^+ sputtering yield is 4.5, our measurements of the sputtering yield ratios are systematically 30-40% low. This is a reasonable value for the possible transmission loss over the amount of time required to perform these experiments. Note that if the atom sputtering yield ratio is measured low, so are the cluster yield ratios. The correction would bring the cluster yields from Ne^+ bombardment to within the experimental uncertainty of the Ar^+ bombardment measurements.

A possible implication of these results is that a more accurate measurement of the sputtering yield of a metal can be made by measuring the size distribution of the clusters than by measuring atom signal ratios. Much further data on the sputtering of different metals by various primary ions is required before this conclusion can be firmly stated.

Summary

Relative sputtering yields of copper atoms and clusters were measured under Ne^+, Ar^+, and Xe^+ bombardment of polycrystalline copper at 3.9 keV and normal incidence. The ratios of the resonantly ionized copper atom signals, corrected for ion current and laser power, gave Ne^+/Ar^+ and Xe^+/Ar^+ sputtering yield ratios of 0.56 and 1.08, respectively. The size distribution of the clusters for the three primary ions showed the expected trend in signal intensities, $Ne^+ < Ar^+ < Xe^+$. The power law fits to the size distributions gave exponents of -8.1, -8.2 and -6.2 for Ne^+, Ar^+ and Xe^+, respectively. The sputtering yield ratios and the size distributions give conflicting results on the relative sputtering yields of copper under bombardment by Ne^+, Ar^+, and Xe^+. The conflict can be resolved by assuming a systematic error in the sputtering yield

ratio measurements that makes the measurements lower than the true values. If a value at the high end of the experimental Ne^+ sputtering yield range is assumed, the exponents of the power law fits agree very well with the previously reported linear dependence on the total sputtering yield.

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Figure Captions

Fig. 1 Relative signal intensities of copper clusters sputtered by 3.9 keV Ne^+, Ar^+, and Xe^+ bombardment of polycrystalline copper as a function of cluster size. All signals normalized to the atom intensity from Ar^+ bombardment. Filled triangles: Ne^+ bombardment; Open circles: Ar^+ bombardment; Slashed squares: Xe^+ bombardment.

Fig. 2 Relative signal intensities of one-photon-ionized copper clusters sputtered by 3.9 keV Ne^+, Ar^+ and Xe^+ bombardment as a function of cluster size, showing power law dependence. Filled triangles: Ne^+ bombardment; Open circles: Ar^+ bombardment; Slashed squares: Xe^+ bombardment; Lines: best least squares fit to power law.

Fig. 3 Exponents of power law fit to size distrubions as a function of total sputtering yield, showing linear dependence. Dotted squares: data from different metals, Cu and Al from ref. [10], Ag and In from refs. [15] and [13], respectively; Filled circles: this work, assuming the highest value for the sputtering yield from Ne^+ bombardment; Line: best least squares fit to linear dependence; Error bar: experimental range of Ne^+ bombardment copper sputtering yields.

Fig. 1

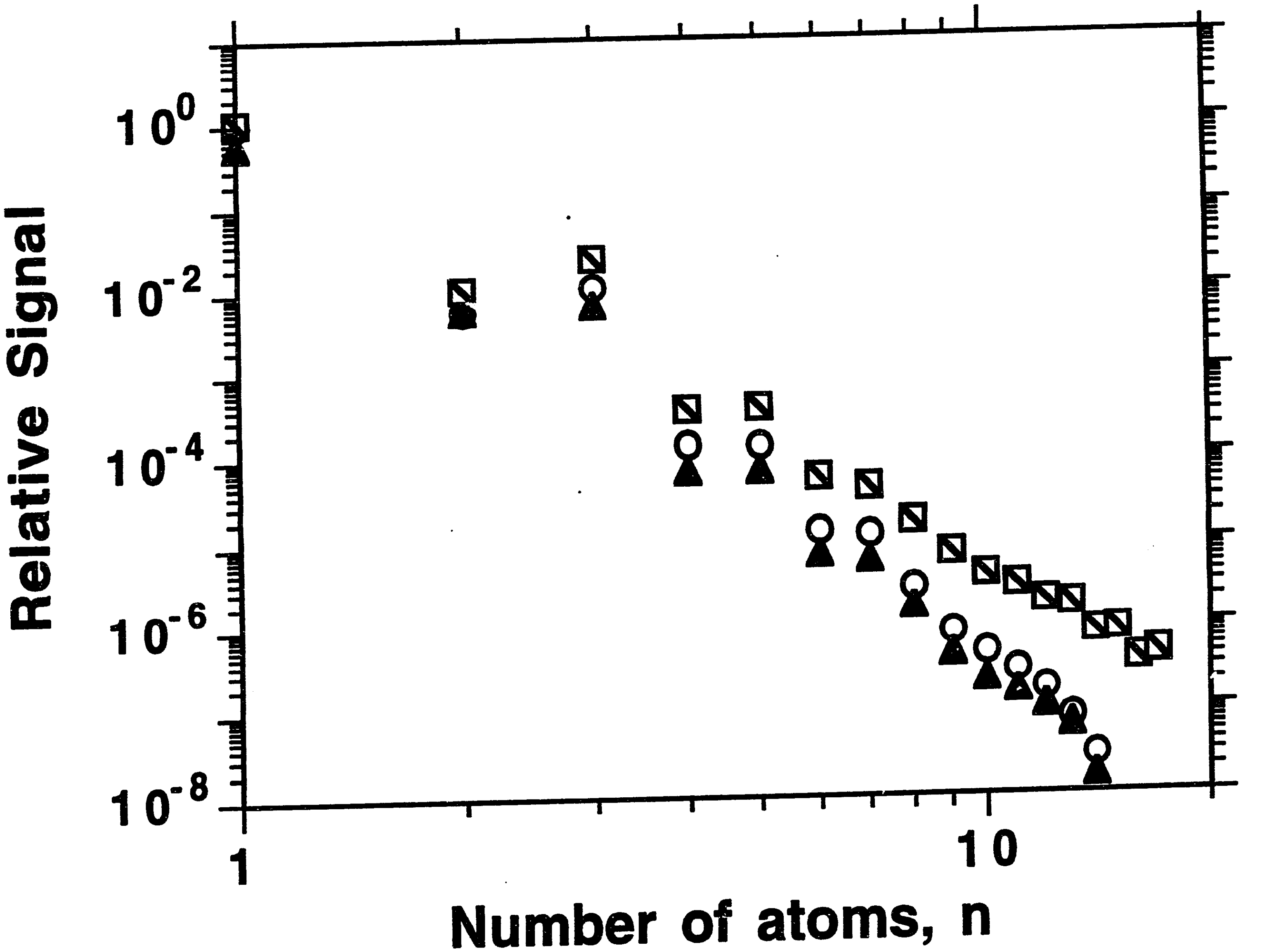
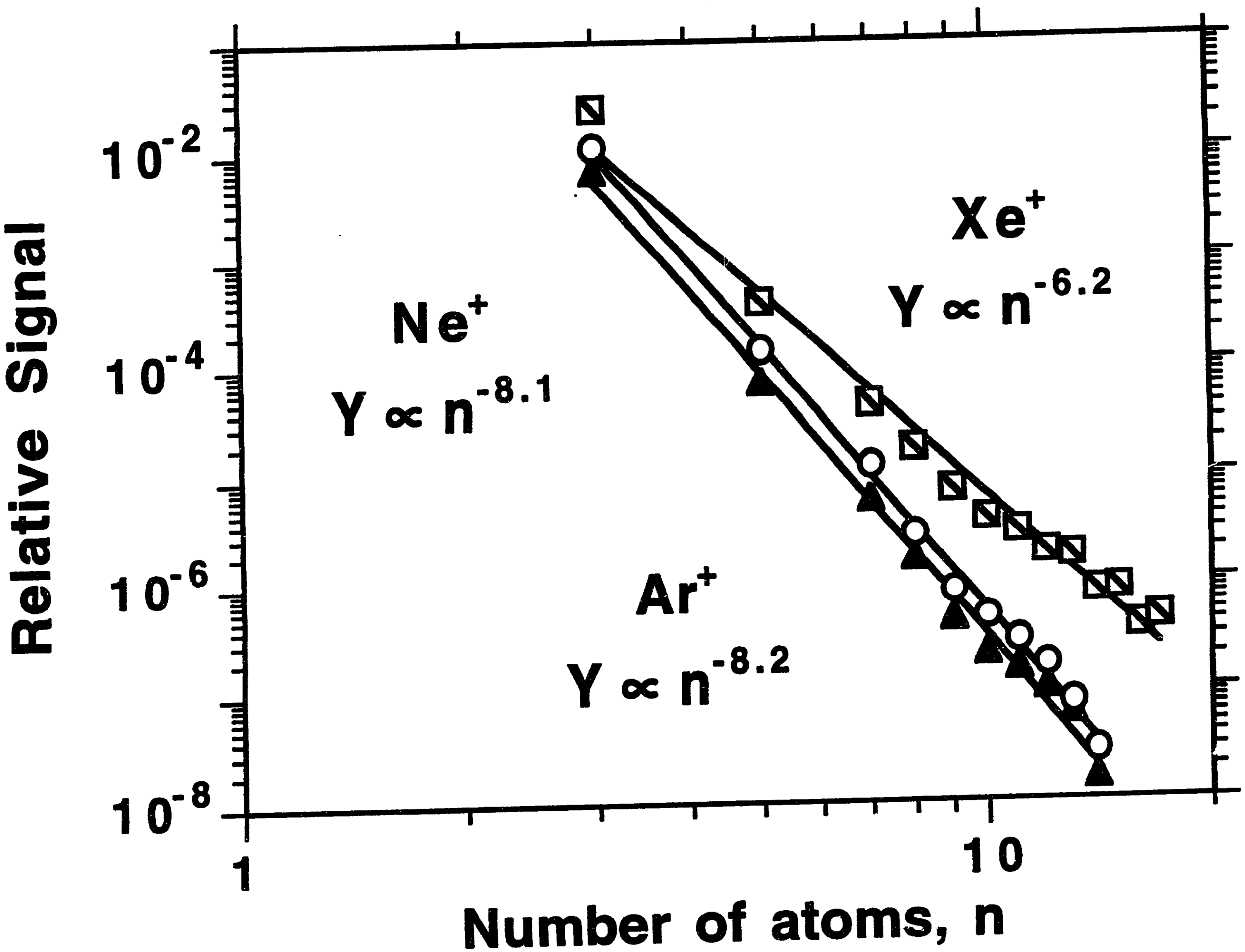


Fig. 2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10^{-4}
10^{-6}
10^{-8}
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10
Number of atoms, n
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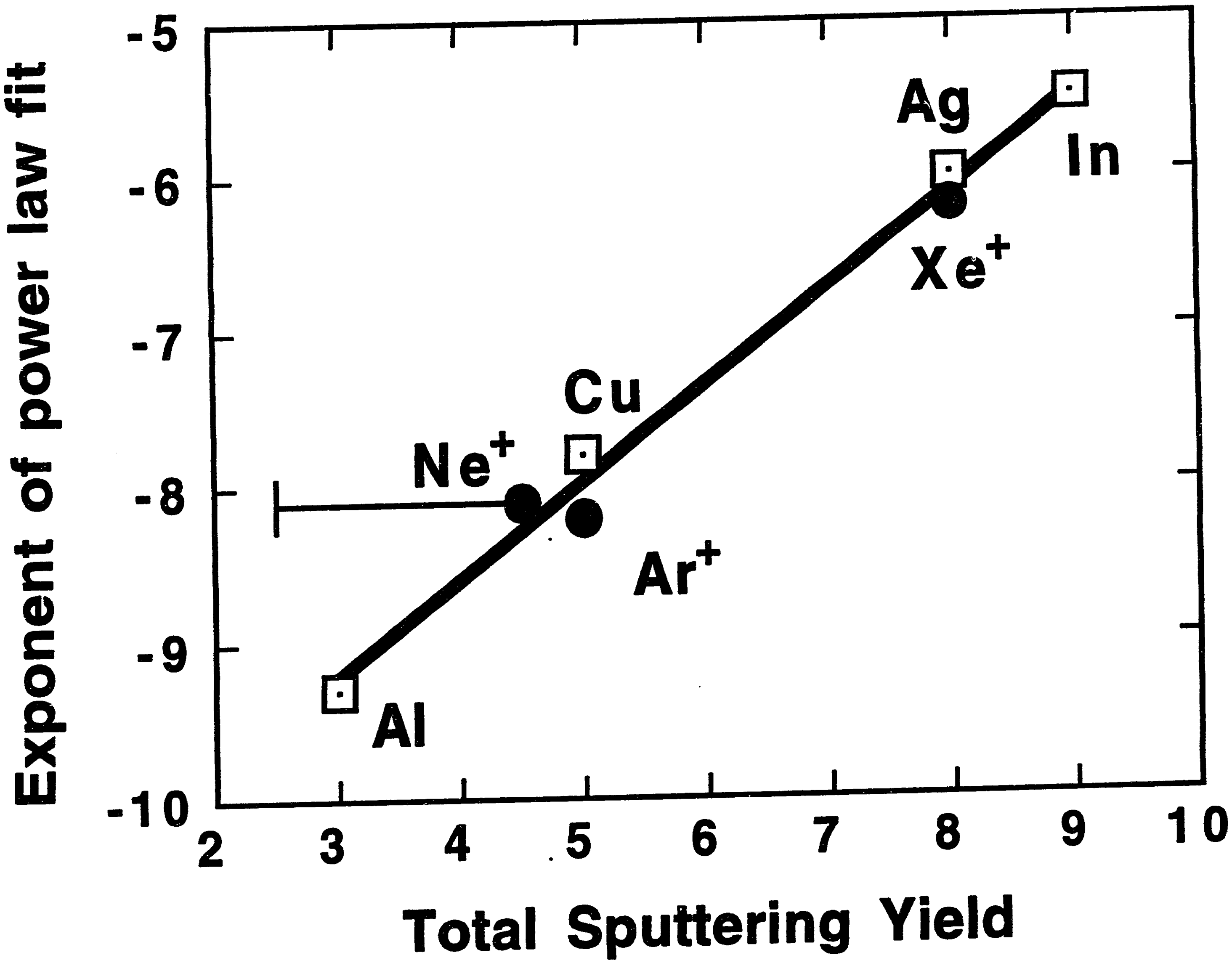
$Y \propto n^{-6.2}$
Ne^+
$Y \propto n^{-8.1}$
Ar^+
$Y \propto n^{-8.2}$

Fig. 3


Exponent of power law fit
Total Sputtering Yield
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