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Formation of negative ions in Cs sputter sources

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Abstract

A surface ionization model with three body interaction is used to explain the mass spectra of negative ions from Cs sputter sources as well as their time dependence. The importance of the high diffusion rate from radiation damaged volumes is illustrated and the difficulties these may cause in quantitative mass spectroscopy with Cs sputter sources are discussed. The anomalously large emittance of single negative ions compared to clusters is ascribed to the surface formation and breakup of negative dimers. An example of negative molecule formation which does not proceed by a surface reaction is given.

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Cs sputter sources are commonly used to produce negative ion beams for injection into tandem electrostatic accelerators. Cs vapor is ionized by contact with a W surface, either through a porous ionizer as in the inverted sputter source¹ or on a helical W wire as in the SNICS ion source.² Positive ion emission from a surface occurs when the ionization potential of the element is smaller than the work function of the ionizer surface. Only Cs, Rb and K meet this condition for a clean W surface and consequently the Cs⁺ beam should not have impurities other than Rb⁺ and K⁺ which if at all present are quite small. For surface ionization to occur, the kinetic energy of the Cs atom when it strikes the ionizer surface should exceed the work required to remove a Cs atom from the surface. At temperatures below 640°K any Cs atom which strikes a Ta surface will remain on the surface.³ Customarily the W ionizer surface in Cs sputter sources is operated near 1200°K.

The modified inverted source⁴ and SNICS are very similar except for the choice of ionizer. Both sources are used at the Argonne ion source test facility.⁵ The Cs⁺ beam is focussed to a spot about 1 mm FWHM at the surface of the sputter target. The Cs beam spot size is one of the determining factors in the emittance of the source² and it is desirable to have an emittance no larger than the acceptance of the accelerator.

The sputtering process has been described by Andersen.⁶ For every Cs projectile which strikes the sputter target, a few atoms will leave the surface. Geometrically it is unlikely that negative ions will exist within the sputter surface therefore one expects the transformation of an emerging atom A into a negative ion A⁻ to occur at or near the surface with



where EA is the electron affinity.⁷ A negative ion can obviously only be formed if EA is positive. In some cases where the element does not have a positive EA, an excited state with a positive EA with a long enough lifetime to reach the tandem terminal ($> 1\mu$ sec) may exist (He, Ca). A simple relation between EA and negative ion beam intensity does not exist but the beam intensities of elements with large EA are usually much higher than those with low ($< 1\text{eV}$) EA.

For the negative ion A^- to survive before it decomposes again into A and e it has to dispose of its excess energy AE. The radiative capture cross section is small and the most likely process is a three body reaction. The density of neighboring atoms will be highest at the surface and this suggests that negative ion formation is a surface ionization process.

The negative ion beam intensity depends strongly on the surface work function which in turn depends on the Cs coverage of the sputter target surface.^{8,9} The Cs coverage of the sputter target is determined by the arrival rate of Cs at the surface and the evaporation rate.¹⁰ The arrival rate is composed of the sputtered implanted Cs atoms with insufficient energy to leave the surface and the diffusion of implanted Cs out of the radiation damaged area. The temperature of the radiation damaged area will be sufficiently high from the energy deposited by the Cs^+ beam and the radiative heat from the nearby ionizer to result in an enhanced diffusion rate. It is improbable that at equilibrium the Cs coverage of the surface will correspond to the minimum in the work function which produces the optimal conversion of neutral to negative atoms. Becker³ has shown that one can increase the Cs coverage by increasing the arrival rate. If one were to do this by increasing the partial pressure of Cs in the source the source would quickly become unoperable. However, one can make use of the fact that work is required to

remove a Cs atom from the surface. We have shown¹¹ that adding Cs to the face of the sputter target with a neutral directed Cs jet can increase the Cs coverage of the target sufficiently to increase the beam intensity tenfold for elements such as Al and Fe, which have a relatively small EA, without an excessive increase in the partial Cs pressure in the source.

The spectrum shown in Fig. 1 was obtained with the SNICS source at a Cs^+ bombarding energy of 2.5 KeV with a Sn target of better than 99% metallic purity. The peaks from mass 112 to mass 124 are due to Sn^- . The relative intensities of the peaks are in good agreement with the isotopic composition of Sn. One notes the presence of small amounts of Al (AlO^- at mass 43, Al_2^- at mass 54, Rh (mass 103) and Ag (mass 107 and 109). The Cu^- component (mass 63 and 65) probably comes from the target holder. The group near mass 150 has an intensity distribution corresponding to the Sn isotopic composition and is probably Sn Al^- . After about 24h a peak appeared at mass 75 and at the same time a group with the Sn isotopic signature appeared at mass $\text{Sn}+75$. Presumably there was a small occlusion of As in the Sn sample. It is surprising that the As^- intensity is only 1% of the observed As. The Sn As^- is expected to be formed at the surface and, in analogy with CN^- , to be quite stable. A possible explanation for the strong Sn As^- peak can be as follows: The largest fraction of the sputtered As will wind up as atoms in the radiation damaged Sn and hence have a high rate of diffusion. A fraction of the As arriving at the surface will stay on the surface as As^- . This is plausible since Becker³ observed that Cs on an oxygen coated Ta surface appeared to be attached as Cs^+ . To retain an electrically neutral surface a corresponding number of O atoms on the surface should be there as O^- ions. The As atoms on the surface can leave as As^- ions by knock-on from emerging sputtered Sn atoms. However, it is apparent that the reaction $\text{Sn} + \text{As}^-$ to

Sn As⁻ is much more likely. Obviously if one were to calculate the As contamination solely on the basis of the As⁻ intensity the contamination would be severely underestimated.

In an experiment with a high purity Mo target after about 2 h the negative ion mass spectrum obtained was the one shown in Fig. 2a with the intensities in the mass spectrum corresponding to the isotopic composition of Mo. The four groups in Fig. 2a correspond to Mo O⁻, Mo O₂⁻, Mo O₃⁻ and Mo O₄⁻. After 6 h of operation the spectrum had changed to the one shown in Fig. 2b. One sees the emergence of Mo⁻ ions while the relative intensity of Mo O⁻ has increased substantially compared to Mo O₂⁻ and Mo O₃⁻. The Mo O⁻ spectrum, however, is now mixed with the Mo C⁻ spectrum. After 24 hours of operation the ⁹⁸Mo⁻ beam had an intensity of 40 nA, the ⁹⁸Mo O⁻ beam of 100 nA and all others were substantially smaller. It appears that in the initial operation there are several layers of O on the surface, in part possibly as negative ions. The outer O layers are less tightly bound than the first O layer which has a strong binding to the Mo surface. The excess O on the surface is apparently cleaned by the emerging sputtered Mo beam and possibly in part by evaporation due to the volatility of the molybdenum oxides¹². After the cleaning of the surface a fairly constant intensity distribution of the Mo⁻ and Mo O⁻ beams persists. It is plausible that similar problems with oxygen layers may also occur with other target materials such as Pb which show, if one considers their EA, an unexpectedly weak negative ion beam.

The emittance of a Cs sputter source according to Billen² is in principle determined by the spatial distribution of the bombarding Cs⁺ beam as it arrives at the sputter target and the angular distribution of the neutral sputtered ions, which one might assume to be similar for different target materials if one uses the same Cs⁺ energy. In an experiment with the inverted

sputter source with an incident beam of 12 keV we measured emittances in the one dimensional transverse direction (x, x') using the emittance measuring device developed by Billen.¹³ We measured not only the emittances of single negative ions but also those of the compound molecules and clusters coming from each target within the mass range of our instrumentation.

If one assumes that the C clusters C_2^- through C_7^- and Al_2^- are representative of the emittance based on Billen's assumptions one can take the average of the measured emittances of these beams measured in (x, x') at the 50% brightness level and compare this average to the measured emittance of the single negative ions. The ratio of the emittances of C^- , Al^- , $^{56}Fe^-$, $^{58}Ni^-$, $^{63}Cu^-$ and $^{65}Cu^-$ to this averaged cluster emittance is shown in Table I. The ratio is in all cases greater than 1. Also the emittances of $^{27}Al^-$, $^{56}Fe^-$, $^{58}Ni^-$ are larger than the emittances of their oxides. That emittance ratio is about 1.5. This effect might be explained by a mechanism similar to the one which we used to explain the Sn As⁻ beam intensity.

The dissociation energy of CC^- is approximately 8.5 eV¹⁴ and is probably one of the largest dissociation energies for negative dimers. Dimers such as C_2 and Al_2 have a substantially larger EA than the corresponding single atom. Values for other dimers are not readily available. If a fraction of the atomic negative ion beam were due to the breakup of a negative dimer, or for that matter of a larger negative cluster, the negative-ion would receive an additional transverse momentum which would result in an increased transverse emittance. On the other hand the negative ion's initial energy would be decreased.

Negative hydrides can be produced with considerable intensity from elements which have no or very small positive EA by introducing ammonia near the sputter surface. If this hydride formation through ammonia were also a surface ionization effect one could minimize the partial ammonia pressure by use of a

neutral jet directed towards the surface. Strasters attempted such an approach in the modified Aarhus sputter source¹⁵ with an Al sputter target. In that experiment the introduction of the ammonia jet decreased the intensity of all negative Al beams including AlH^- by about 20% while producing a $16 \mu A NH_2^-$ beam.¹⁶ This suggests that the formation of hydrides such as $Al H^-$, $Ca H_3^-$ and $Mg H^-$ occurs in the gas phase and not immediately at the sputter target surface.

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TABLE I. Ratio of one dimensional transverse emittance of single negative atoms to the corresponding average emittance of negative clusters at the 50% brightness level.

Element	^{12}C	^{27}Al	^{56}Fe	^{58}Ni	^{63}Cu	^{65}Cu
Ratio	1.2	2.3	2.6	1.6	2.0	2.0
Emittance (π mm mrad MeV ^{1/2})	2.85	4.15	4.60	2.85	3.6	3.6

Figure Captions

Fig. 1 Negative ion mass spectrum obtained from a Sn target with a small As occlusion.

Fig. 2 Mass spectra of negative ions from a Mo sputter target a) after 2 hours of operation, b) after 6 hours of operation.

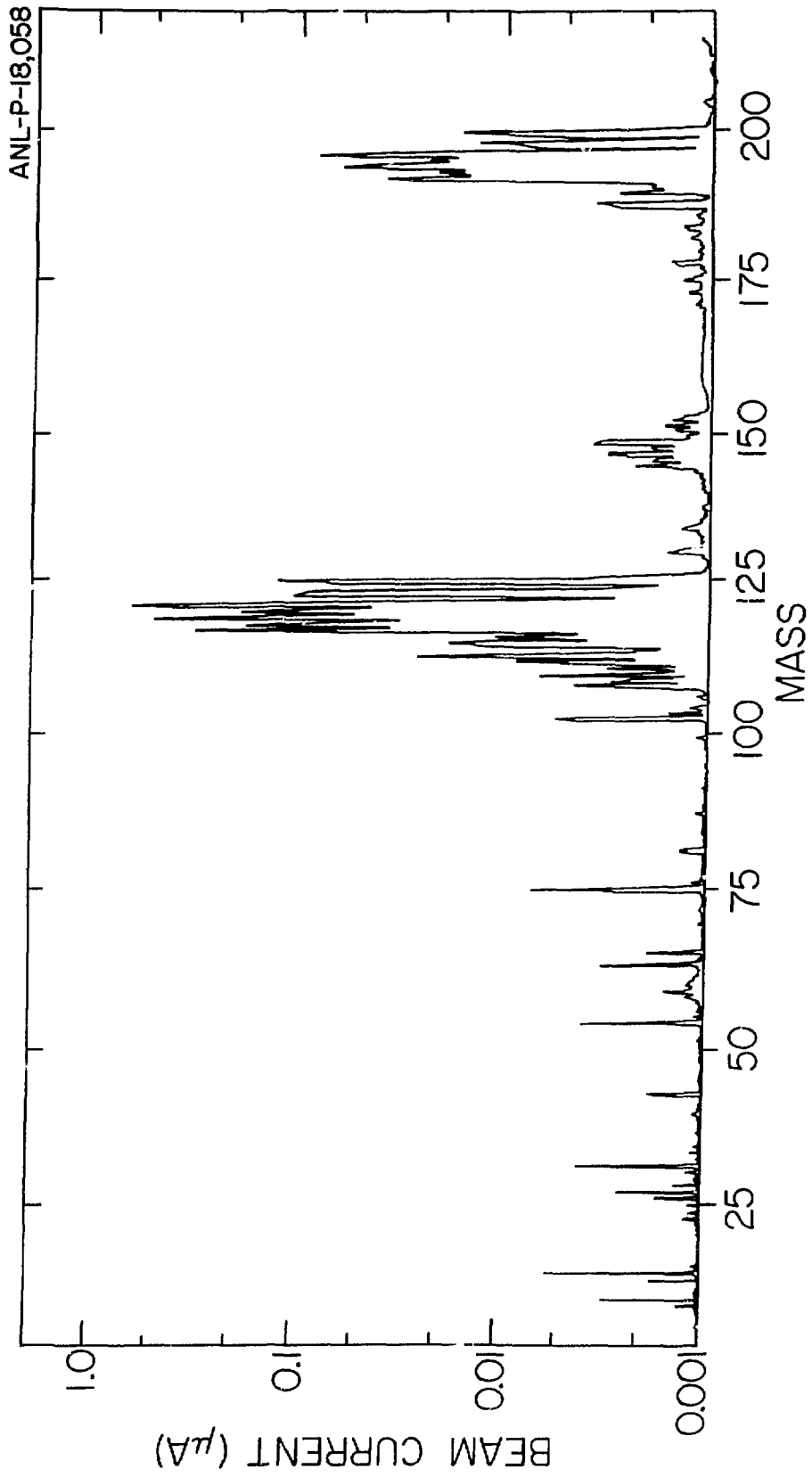


Fig. 1

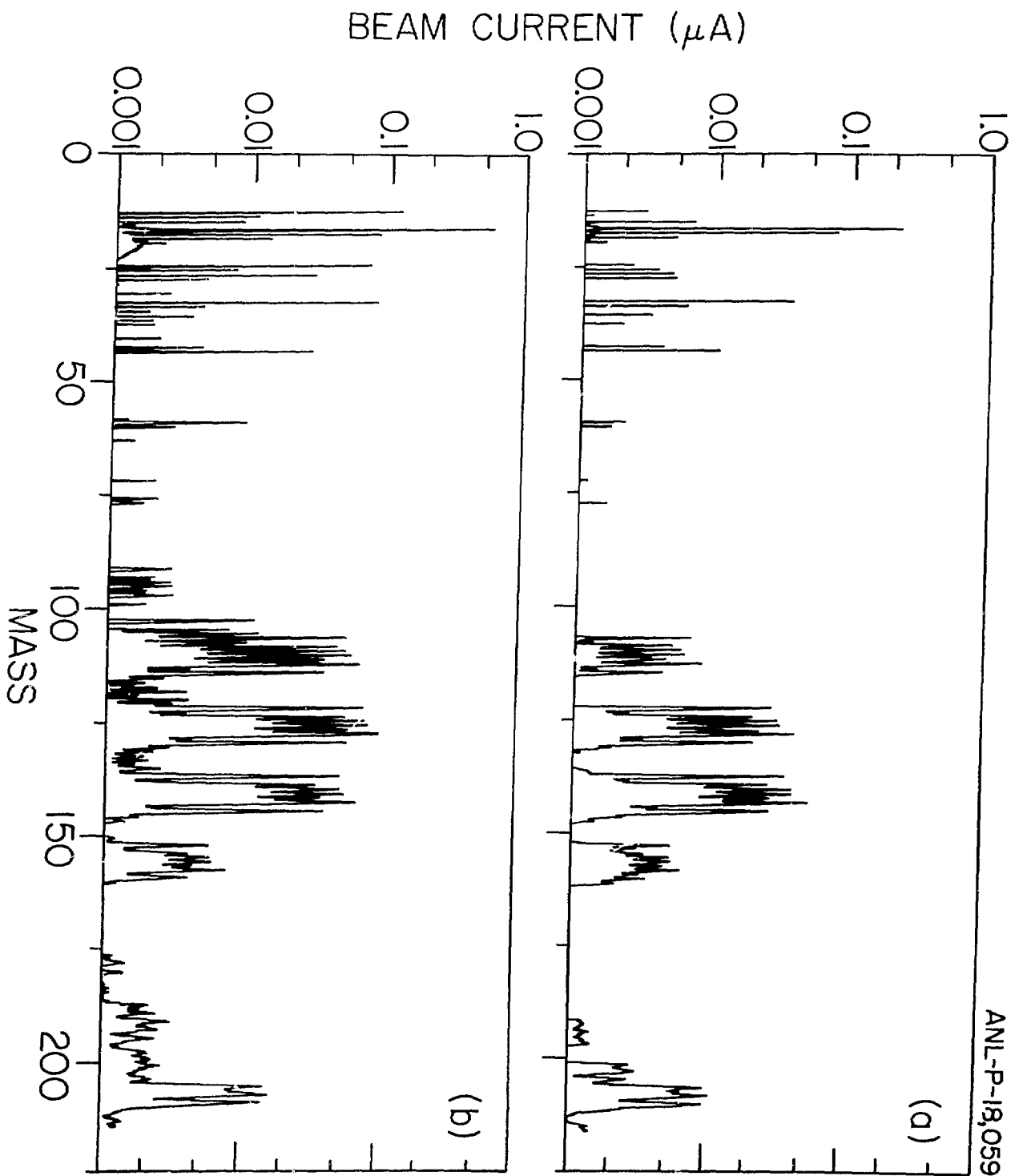


Fig. 2