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TECHNICAL REPORT

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THIN FILM ANNEALING BY ION BOMBARDMENT

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S U M M A R Y

The enhancement of film adherence resulting from argon ion bombardment during the evaporation procedure has been studied experimentally. The observations point to the existence of an annealing effect caused by atomic rearrangement in bombardment induced temperature spikes. This mechanism begins to be effective at a critical minimum bombardment intensity, which is sufficient to ensure that practically all the deposited material is subjected to rearrangement soon after it has condensed. The small amount of argon incorporated into the film by the bombardment is shown to have no significant influence on the process.

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1. INTRODUCTION

In an earlier publication(ref.1) it was reported that the substrate adherence of vacuum evaporated Germanium films could be substantially improved by performing the deposition under simultaneous bombardment with argon ions. In this way it proved possible to maintain the mechanical integrity of films that under their high intrinsic stress would otherwise have cracked into small fragments, which would become readily detached from the substrate. The earlier experiments indicated that two distinct bombardment induced mechanisms tended to produce this enhanced adherence. The first of these appeared to be an effect associated with the film-substrate boundary, causing a strengthening of the interfacial bonding through the formation of a transition layer, where the composition of the material was intermediate between that of the film and of the substrate. In addition to this, a second effect was shown to be associated not with the interface but with the film itself. From the manner in which it also inhibited cracking and lifting, it was considered to act through a reduction in the intrinsic film stress, but for this stress diminution to occur the ion current density had to have at least a critical minimum value I_c.

The present work is concerned with this second "annealing" effect, and it aims at its explanation by examining the ion energy dependence of I_c, together with the possible role played by the incorporation of argon into the film material, a phenomenon unavoidably associated with the ion bombardment.

2. EXPERIMENTAL METHOD AND RESULTS

Germanium fims were deposited on Tempax glass substrates, using the apparatus previously described(ref.1). Since we were interested only in "annealing" within the film proper, the bombardment induced interface effect was inhibited by initially laying down a non-irradiated Ge film of 1000 Å thickness. As discussed in the earlier work, this acted as a barrier to all ions in the energy range used, and so prevented irradiation of the interface. On this barrier layer a 2 μm Germanium film was deposited at a rate of about 2.2 Å/s, under simultaneous ion bombardment. In the absence of sufficient irradiation, films of this thickness were known to exhibit severe cracking and flaking from the substrate.

A movable Faraday cage permitted determination of the radial current density distribution in the ion beam, which was dependent on the ion energy as well as on the total beam current. A typical example of this distribution is given in figure 1, where it is seen that the intensity fell smoothly from a maximum at the beam centre towards zero at large radial distances.

For film deposition at any ion energy E the beam current was adjusted so that the current density on the beam axis was well in excess of the critical minimum value I_c, ensuring that at some radial distance r_c this critical level would in fact be attained. For $r \leqslant r_c$ the stress "annealing" mechanism was effective, the film remained intact and adhered well to the substrate, whilst for $r > r_c$ the irradiation intensity was insufficient to prevent the film from cracking and lifting off in the manner previously shown in figure 3 of reference 1. The transition between good and inadequate adherence was sufficiently abrupt to allow r_c to be measured to about $\pm$ 0.1 mm. The corresponding critical current I_c could then be obtained from the beam intensity profile.

Through a series of measurements of this type, covering a range of ion energies, the relation between I_c and E was determined, and the results are shown in figure 2, where it is seen that in the range from 65 eV to 3000 eV the

critical current density is well approximated by

$$I_c \simeq \frac{6.2 \times 10^3}{E^{3/2}} \ \mu A/cm^2 \equiv \frac{3.9 \times 10^{16}}{E^{3/2}} \ \text{ions/cm}^2/\text{s} \qquad (1)$$

There was thus a steady increase in the critical argon ion current density as the beam energy was lowered. A fraction of the impinging ions became incorporated in the growing Germanium film, and the total amount of argon occluded at any particular point of the completed deposit could be determined by means of an electron microprobe. It was found that at constant current density the argon uptake diminished at an accelerating rate with decreasing ion energy (see figure 3(a)), but as figure 3(b) shows, when E was kept constant, the quantity of occluded argon was directly proportional to the ion current density. In view of this linear relationship, and since the microprobe photon count rate in film areas that had received only the critical current density was rather low, the count rate P_c corresponding to I_c was derived by obtaining the maximum count rate on the beam axis, and multiplying it by the appropriate current ratio. Figure 4 shows P_c arrived at in this manner as a function of the ion energy. In the absence of a quantitative calibration of the microprobe it is expressed as a fraction of the count rate for Germanium, the principal constituent of the film. The curve of figure 4 is seen to pass through a maximum, since at high energies, the correspondingly low values of the critical current density lead to a small uptake of argon, whilst at low energy the increase in I_c is counterbalanced by a rapid decrease in the occlusion probability.

3. DISCUSSION

In making use of our results to gain additional insight into the nature of the "annealing" mechanism, we recall that as an incident ion comes to rest, a substantial portion of its energy is transferred to lattice vibrations of neighbouring atoms, which in this case are nearby atoms in the growing Germanium film. In the course of this, the local temperature in a small region of the material is raised for a brief period to values sufficiently high to cause permanent rearrangement of the atoms(ref.2,3,4), and we suggest that the "annealing" is a consequence of this atomic movement, that may be pictured as an interdiffusion in the temperature spike.

Using a somewhat idealised model for the spatio-temporal development of the temperature pulse, Seitz and Koehler (loc.cit. p 359) have deduced the number of atoms n_T participating in an activated rearrangement process during the life time of the spike to be given by

$$n_T = 0.016 \ \rho \left(\frac{Q}{E_1}\right)^{5/3} \qquad (2)$$

where E_1 is the activation energy of the process, and Q is the energy deposited in the spike by the incident particle. Some uncertainty is attached to the numerical value of the coefficient ρ, which depends on material parameters such as the thermal diffusivity and atomic volume, as well as on the number of symmetrically equivalent neighbours with which an atom can interact, but according to Seitz and Koehler ρ should lie in the range from 1 to 10.

As regards the amount of energy Q deposited in the spike, we shall for simplicity ignore the possibility of cascade effects and assume each incident ion to produce only one temperature spike. Then, inserting for Q the incident ion energy E we obtain

$$n_T = 0.016\,\rho\left(\frac{E}{E_1}\right)^{5/3}. \qquad (2(a))$$

At an ion flux of I_c ions/cm^2/s the number of target atoms involved in interdiffusion or a similar rate process during a spike will then be $I_c n_T$ atoms/cm^2/s. According to equation (1) I_c varies approximately as $1/E^{3/2}$, but the effect of replacing the empirical exponent 3/2 by 5/3 is numerically not very significant (see dotted line in figure (2)), and making this substitution one finds from equations (1) and (2(a)) that the total number of atoms involved

$$I_c n_T = 6.2 \times 10^{14}\,\frac{\rho}{E_1^{5/3}} = \text{const.} \qquad (3)$$

i.e. within the limits of our approximation the critical current density varies with ion energy in such a manner that the rate at which atoms can undergo rearrangements in a temperature spike, remains constant. Moreover this constant rate appears to be comparable in magnitude with the rate of arrival R of Germanium atoms at the substrate. Assuming the film to have bulk density (5.32 g/cc), a deposition rate of 2.2 Å/s implies that R = 9.7 x 10^{14} atoms/cm^2/s. Inserting this for the constant term on the right hand side of equation (3) one obtains that

$$\frac{\rho}{E_1^{5/3}} \approx 1.6 \qquad (4)$$

We have made no detailed assumptions concerning the nature of the postulated rearrangement processes, and therefore cannot assign a definite value to the activation energy E_1, but by introducing typical values into equation (4) we can show that it is readily satisfied, in the sense of yielding values for ρ in the expected range $1 < \rho < 10$. For example, adopting E_1 = 1.78 eV as the activation energy for the diffusion of vacant lattice sites in Germanium(ref.5) we obtain $\rho \approx 4.2$, whilst E_1 = 2.97 eV, corresponding to the case of self diffusion(ref.6) leads to the equally acceptable value of $\rho \approx 4.75$. From these considerations arises the intuitively plausible inference that the "annealing" effect becomes apparent at a critical current density I_c such as to ensure that practically all the incident Germanium atoms are subjected to an activated rearrangement process in a thermal spike*.

The "annealing" is however not significantly affected by the bombardment induced uptake of argon, and figure (4) indicates that there is no critical argon content level that marks the onset of enhanced film adherence. In agreement with the measurements of Winters and Kay(ref.7) on argon incorporation in nickel films, the gas content in the present work was found to become progressively less as the particle energy was lowered, and it ceased to be detectable in the vicinity of 100 eV. Nevertheless film adherence continued to be enhanced down to energies well below 65 eV, where gas incorporation was extremely small. However, whilst it was possible to establish the existence of unimpaired enhancement in this range of very low beam potential, space charge instabilities

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* At the energies used in the present experiments the ion range was of the order of only a few Å. Temperature spikes would therefore always develop essentially at the surface, where new material was being laid down.

prevented a reliable determination of the critical current.

If our explanation of the "annealing" in terms of atomic rearrangements in thermal spikes is correct, then one would expect the effect to be of a general nature rather than to be a specific property of Germanium. This seems indeed to be the case, since similar behaviour has also been observed in MgF_2, and it is hoped to report in due course more detailed investigations relating to this and other materials.

4. CONCLUSION

From the foregoing results we conclude that when films are deposited by vacuum evaporation under simultaneous argon ion irradiation, annealing of their intrinsic stress takes place through atomic rearrangements in bombardment induced temperature spikes. The small amount of argon occluded in the film during this process does not appear to be a relevant factor in the stress reduction. If however other considerations make it desirable to minimise the argon incorporation, this can be achieved by carrying out the bombardment at the lowest ion energy compatible with the space charge limitations of the apparatus.

5. ACKNOWLEDGEMENTS

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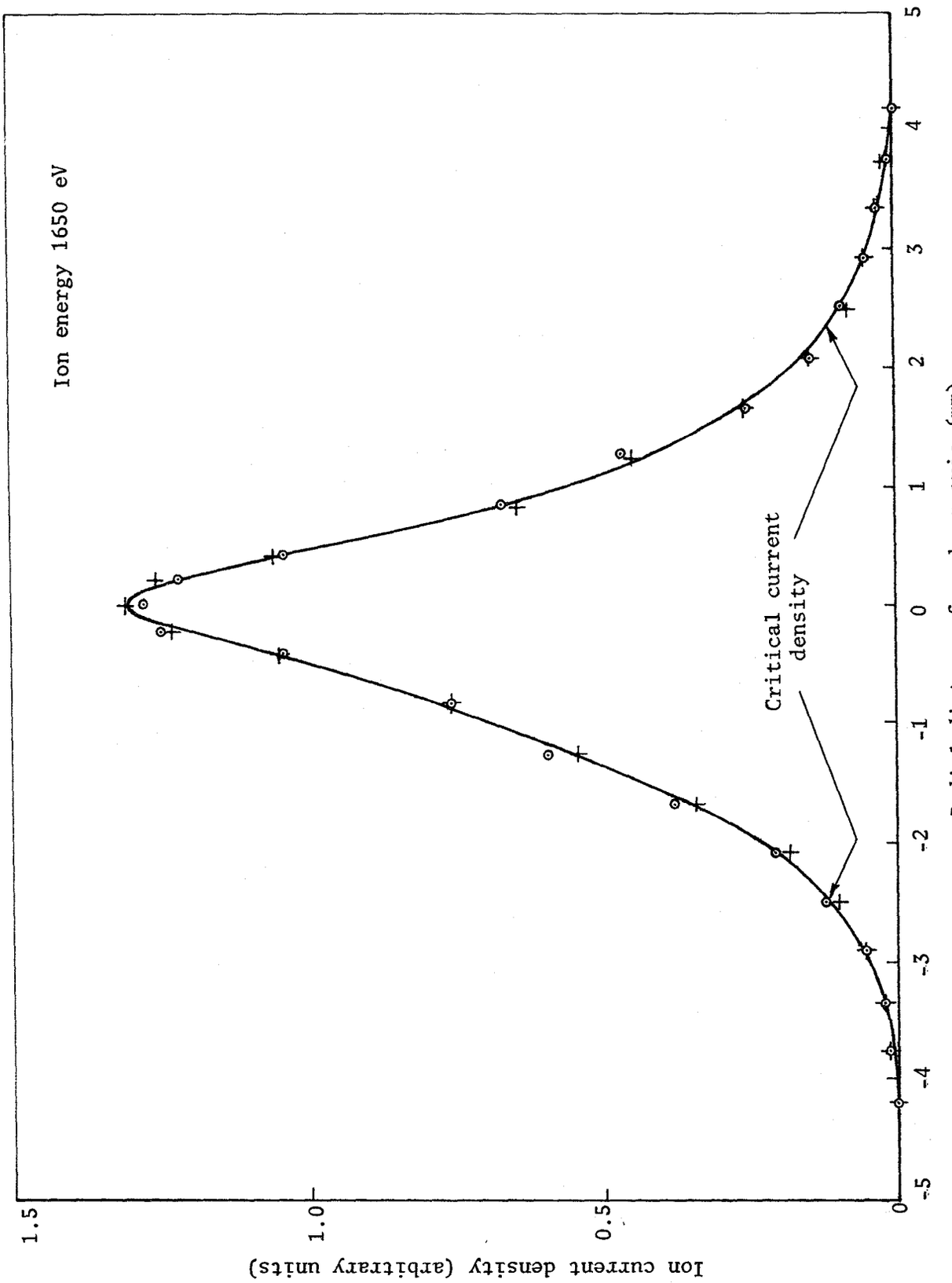

Figure 1. Beam current density distribution

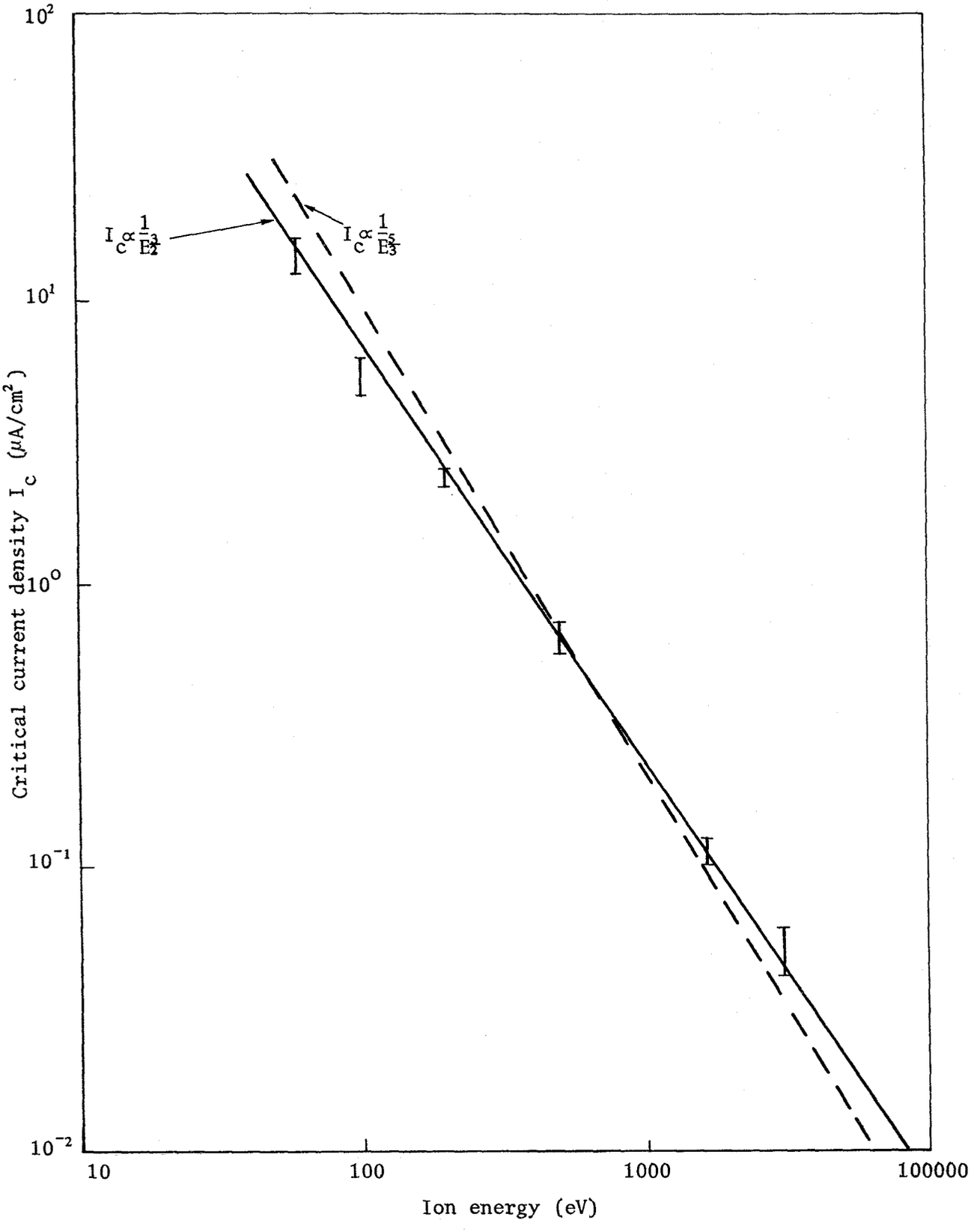

Figure 2. Critical current density as function of ion energy

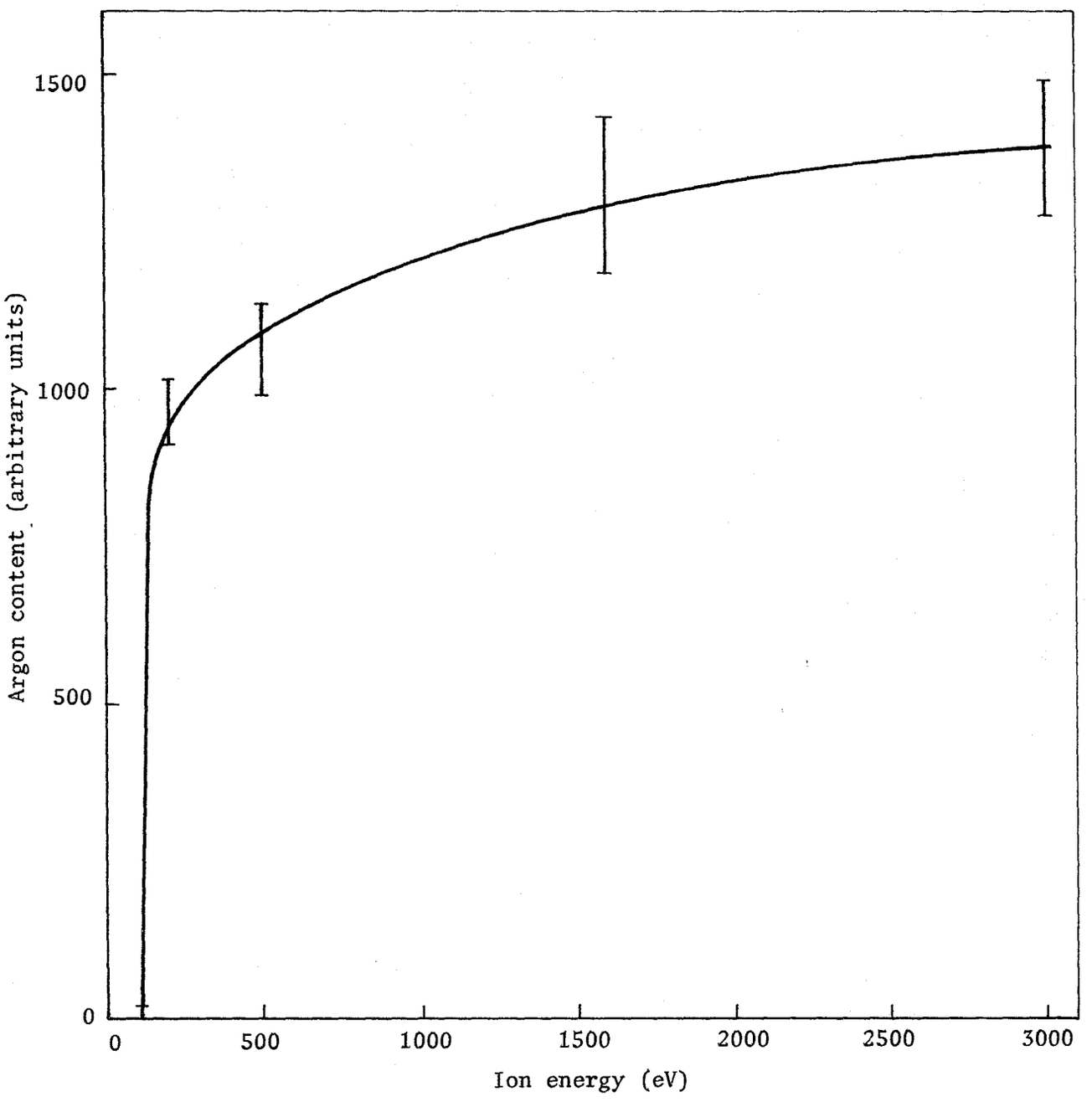

Figure 3(a). Variation of argon content with ion energy

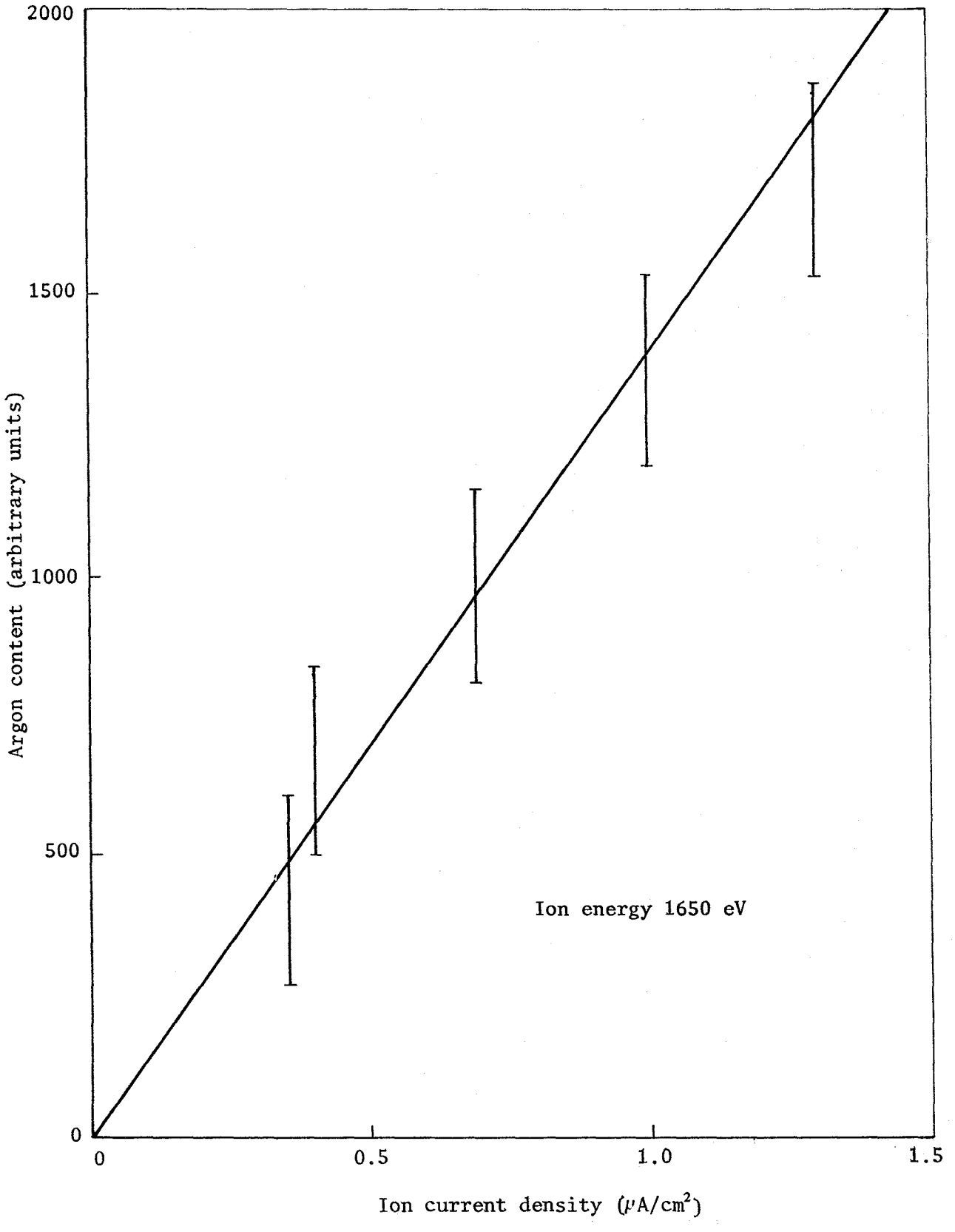

Figure 3(b). Variation of argon content with current density

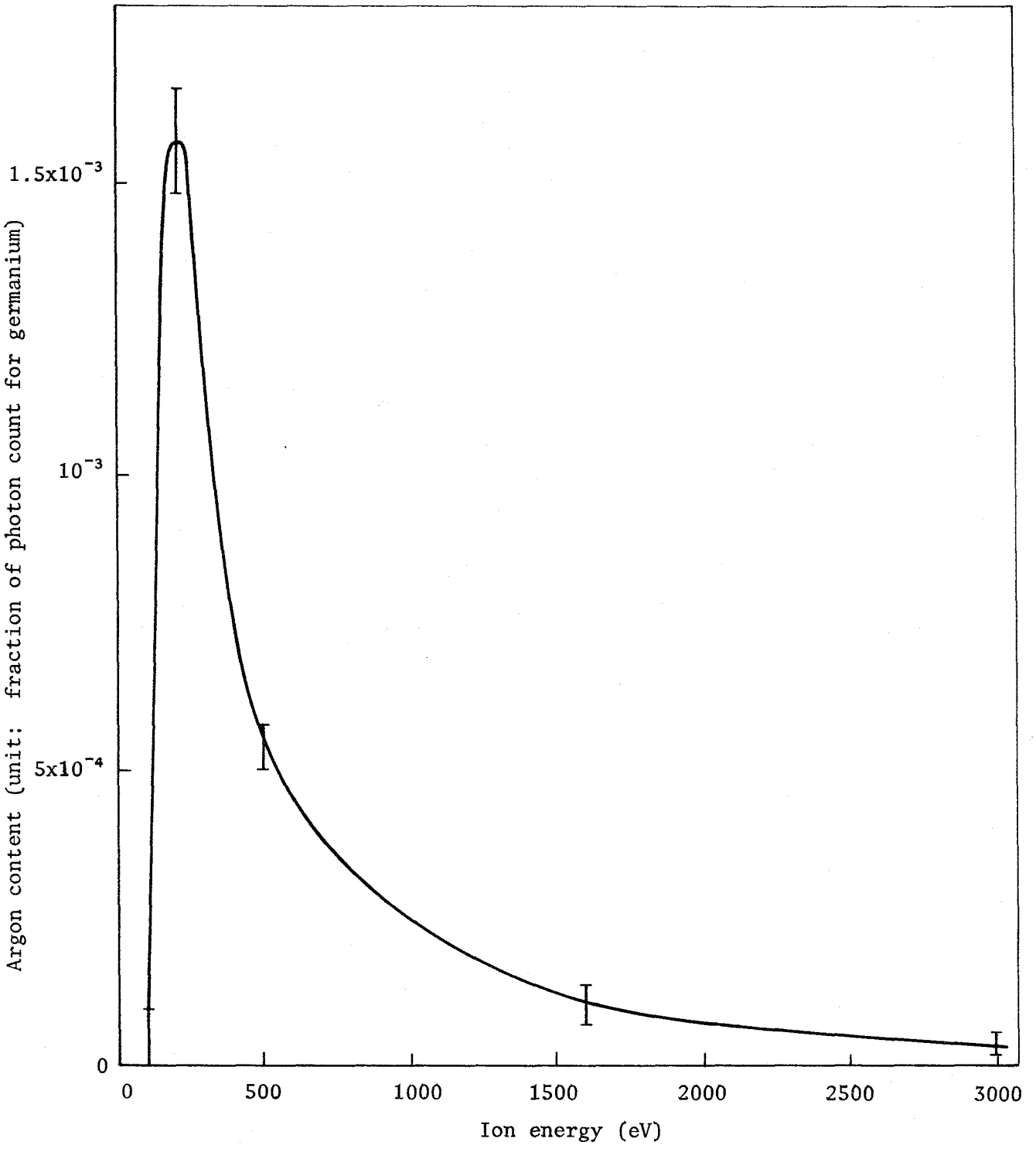

Figure 4. Argon content at critical current density as function of ion energy

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