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E.H. HIRSCH and I.K. VARGA

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THE EFFECT OF ION IRRADIATION ON THE INTRINSIC STRESS AND SUBSTRATE ADHESION OF GERMANIUM FILMS

E.H. Hirsch, M.Sc. and I.K. Varga, B.Tech.

SUMMARY

Irradiation with argon ions is shown to increase greatly the adhesion of vacuum evaporated Germanium films on glass and other substrates. The observations suggest that the effect is due to the penetration of Ge atoms into the substrate after collision with the energetic ions.

In addition, the intrinsic stress of films deposited under ion bombardment is found to be substantially lower than that of similar films, produced without simultaneous irradiation.

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1. INTRODUCTION

Although the adhesion of thin films is a subject of considerable practical interest in the technology of solid state devices, our understanding of the detailed mechanism of film adhesion is far from complete. It is however generally agreed, that for any pair of film and substrate materials the adhesion is dependent largely on the degree of cleanliness as well as on the structure of the surface, particularly on the number of point defects which are present, and which can act as nucleation centres during the early stages of film formation. It has also been widely observed(refs.1,2,3) that adhesion of sputtered films is often superior to that of films produced by vacuum evaporation. As pointed out by Mattox and McDonald(ref.2), this enhanced adhesion is intuitively plausible in view of the fact that the sputtered atoms arrive at the substrate with energies well in excess of thermal, with values lying typically in the range of some tens of electron volts or more. These energies are sufficient to cause the removal of surface impurities by sputter etching, and to produce additional nucleation sites through the displacement of atoms in the substrate lattice. There is also the possibility that energetic incident particles will penetrate some distance into the substrate, and in so doing will enhance the adhesion by the formation of a transition region between the materials of the substrate and of the film. Finally there are instances(refs.4,5) where reactive sputtering may increase adhesion through the formation of oxides.

All these various mechanisms provide possible explanations for the observed increase in film adhesion, but unfortunately they are mechanisms which may all act during sputter deposition with presumably equal likelihood, and under circumstances which make it practically impossible to isolate them experimentally, so as to assess their relative importance and to control in detail the diverse aspects of the deposition process.

In contrast to this, such isolation of the relevant factors can be achieved in the experiments to be described below, which are concerned with the properties of Germanium films, deposited on glass by conventional vacuum deposition, but in an apparatus, where the impinging Ge atoms could gain additional energy far above the thermal level through collisions with a beam of argon ions, directed on the substrate from a separate source. An arrangement of this type permits both the incidence of neutral atoms, and the transfer of extra energy to them, to be separately controlled. It is the purpose of this paper to show that by systematic changes in the bombardment and evaporation procedures it is possible to vary the properties of films, in particular their adhesion, and to clarify the part played by the various suggested mechanisms in bringing about adhesion enhancement.

2. EXPERIMENTAL ARRANGEMENT AND RESULTS

The experiments were carried out in the apparatus shown schematically in figure 1. Germanium was evaporated from an indirectly heated graphite crucible, surrounded by a series of heat shields. Using a crucible-substrate distance of about 12 cm, and with the substrate surface inclined at an angle of 45° to the axis of the molecular beam, a deposition rate of about 3 Å/s was obtained over an elliptical area having semi-axes of roughly 10 mm and 14 mm respectively. A portion of this region could in addition be irradiated by ions, which, with a beam diameter of approximately 5 mm, were incident over an area of about $0.27\ cm^2$.

To prevent the accumulation of charges on the glass substrate, its surface could be flooded by slow electrons from a tungsten filament, arranged so as to ensure thermal radiation from it could not have an appreciable effect on the substrate temperature. A mechanical shutter permitted control of the molecular beam, whilst the ion current was switched via the anode potential of a hot cathode plasma ion source. The arrangement was mounted in an envelope evacuated by a liquid nitrogen trapped oil diffusion pump, which maintained the pressure in the system at about 4×10^{-6} Torr during a typical deposition run.

In the experiments to be described, the ion beam energy was for convenience adjusted to 1650 eV, although this value was by no means critical. With a beam current of 2 μA the mean ion incidence rate was $4.6 \times 10^{13}/cm^2s$, as compared with an arrival rate of neutral Germanium atoms of $1.3 \times 10^{15}/cm^2s$. The ions thus constituted only 4% of the total particle flux reaching the area covered by both beams, but nevertheless ion irradiation had a profound effect on the properties of the Germanium films.

In the absence of ion bombardment, and as long as the Germanium deposit was reasonably thin, the films presented a smooth mirror finish, but when the thickness reached about 1 μm to 1.5 μm, fracture lines began to appear, and these generally followed a direction roughly parallel to the minor axis of the elliptical film area. At a thickness of 3 μm the intrinsic stress within the film had increased to such an extent that the material was lifted from the substrate in long flakes, tilted from the surface, forming louvre-like structures, as shown in figure 2, with the "louvres" invariably opening towards the evaporation source.

This behaviour changed drastically, if part of the surface was bombarded with argon ions during the evaporation. The deposit was then strongly adherent, and showed no sign of flaking or fracture anywhere on the irradiated area. This is illustrated in the example of figure 3, where it is interesting to note that the region of strong adhesion was sharply bounded, with no obvious gradation in film bonding towards its boundary. This boundary corresponded to the edge of the ion beam, in the vicinity of which the bombardment intensity changed significantly, as seen in figure 4, illustrating the variation of ion current density along the minor axis of the bombarded zone.* From the absence of any detectable difference in film appearance in areas subjected to quite different bombardment intensities, it is clear that the value of the current density is not very critical, and the figure suggests that an ion incidence rate at least an order lower than actually used, might well have been sufficient to produce the observed adhesion enhancement.

It is evident from figure 3 that ion irradiation either causes stronger bonding between the film and its substrate, that it leads to a decrease in the intrinsic film stress, or that it possibly produces a combination of both these effects. We shall for the moment leave aside the question of a diminution of intrinsic stress, and examine first the possible role of the various mechanisms discussed in the previous Section in bringing about enhanced adhesion.

If the removal of surface impurities by ion etching, or the creation of additional nucleation sites were significant factors, one would expect ion irradiation immediately prior to, as distinct from during the actual deposition, to be also effective. However films of 3 μm thickness deposited after such pre-irradiation were indistinguishable from the film of figure 2, prepared without any ion bombardment. An interesting effect of pre-irradiation was however observed when the film thickness was reduced from 3 μm to 2 μm. In these thinner films, when deposited without preceding bombardment, the intrinsic stress, whilst high enough to cause the appearance of some fracture lines, was insufficient to result in actual lifting of the film. In the example of figure 5, showing a pre-irradiated 2 μm film, this is the case on that portion of the substrate, which had received no ions at any stage. In the pre-irradiated area on the other hand the Germanium is seen to have lifted off, indicating that here the adhesion had in fact been markedly lowered by the ion bombardment. We shall return later to this rather unexpected result, and merely note here that according to our observations neither sputter cleaning nor the creation of additional nucleation sites contribute to the strengthening of the bonding. It is also clear that processes such as oxide formation by reactive sputtering are excluded under our experimental conditions.

To achieve increased bonding it is in fact necessary for the energetic ions to interact with the neutral condensing particles in the immediate vicinity of the substrate, and the experimental evidence presented below is consistent with a picture of ion-atom collisions causing Germanium atoms to be projected into the substrate, where they presumably form a transition layer. This conclusion is reached on the basis of a series of experiments, indicated schematically in figure 6.

In the first type of experiment (figure 6(a)) an initial thin film of Ge was laid down under simultaneous ion irradiation, followed by a second much heavier layer of 3 μm to 5μm thickness, produced without ions incident, so that its high intrinsic stress would normally cause it to lift off. This did actually happen everywhere, except on the thin ion irradiated deposit. Here the adherence was excellent, and the appearance of the film could not be distinguished from that of a film produced under ion bombardment during the entire deposition. This was always the case provided the initial irradiated layer was not too thin, a thickness of 700 Å to 1000 Å certainly being sufficient. Even an initial layer of only 50 Å nominal thickness produced strong bonding, although some fracture lines were present, but these were much reduced in extent by approximately doubling the initial thickness.

The adhesion enhancement was however completely prevented by interposing between the irradiated layer and the substrate a very thin non-irradiated Germanium film of about 200 Å thickness. This is readily explained by noting that the mean range of the 1650 eV ions used in the present experiments is only about 15 Å, as derived by extrapolating to lower energies the range values calculated by Sigmund and Sanderson(ref.6) for A^+ ions in amorphous Germanium. The ions thus could not penetrate the 200 Å barrier**, and for enhanced adhesion the Ge atoms clearly interact with the ions close to the substrate.

The interaction does however not require the neutral atoms and the ions to be incident simultaneously. This is shown by the experiment indicated in figure 6(c). Here the initial layer was built up in stages of a few Å thickness, i.e. in layers comparable to the estimated ion range, so that each layer could be suffused by subsequent ion irradiation. In the first instance a step thickness of 10 Å was selected. Bearing in mind the 45° angle of incidence, this represents the approximate distance an ion would be able to penetrate through the Germanium film, although of course a layer of nominally 10 Å thickness will not be uniform and continuous, so that in this context the concept of ion range will be of heuristic value only.

During the 3 s needed to put down the first 10 Å layer, the ion beam was switched off. The vapour stream was then interrupted, and the deposit was irradiated for an equal period of 3 s. The process of alternating deposition and irradiation was repeated until a film of about 700 Å thickness had been built up. The irradiation was then discontinued altogether, and the evaporation allowed to proceed to a total thickness exceeding 3 μm. At this stage the overall structure of the film was analogous to that of figure 6(a) except that now deposition and irradiation were not simultaneous. As before, there was strongly enhanced adhesion, although there was some evidence of fracture lines, which had not been present in the case of simultaneous irradiation. It was therefore decided to repeat the experiment, with ion penetration

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* The current density was inferred from Talysurf measurements of erosion depth on a substrate exposed to the ion beam without vapour deposition.

** A similar conclusion applies if, instead of penetration by A^+ ions we consider the passage of recoil Ge atoms through the film.

made easier by reducing the evaporation time for each individual step from 3 s to 2 s, corresponding to a nominal layer thickness of approximately 6 Å. As a result there was a marked decrease in the development of fracture lines, showing the need for effective penetration of the Germanium layer, and supporting our view that adhesion is primarily enhanced through Ge atoms being enabled to enter the substrate after collision with sufficiently energetic ions.

Finally we must turn to the possibility, briefly referred to earlier, that in addition to causing stronger bonding, ion bombardment may also lead to a lowering of the intrinsic stress in the film, thus lessening its tendency to lift off. In order to examine this question, a 5 μm film was deposited under continuous ion bombardment on a glass substrate, onto which immediately before a 1000 Å Ge layer had been evaporated with the ion beam switched off (see figure 6(d)). The adhesion of the heavy deposit was excellent. To enable a conclusion from this, we recall that on the one hand numerous experiments had shown that in the absence of ion irradiation the stress in a 5 μm film invariably caused fracture and lift off, but that on the other hand the experiment of figure 6(b) had firmly established a 1000 Å Ge layer to be an impenetrable barrier to any adhesion promoting ion interaction at the film-substrate interface. It must therefore be concluded that in this case the heavy deposit failed to lift off not because of strengthened bonding to the substrate, but because its intrinsic stress had been reduced by ion irradiation.

3. CONCLUSION

The experiments described in the previous Section have established that in the enhancement of film adhesion by ion bombardment the creation of additional nucleation sites through ion impact played no significant role. Also ion irradiation of the substrate prior to commencement of the vapour deposition led, presumably through the removal of surface impurities, not to an increase, but to a pronounced lowering of adhesion, in spite of the fact that glow discharge treatment and sputter cleaning are widely used techniques of substrate preparation(ref.7). In assessing this result it will be realised that, whilst substrate "cleanliness" is generally regarded as beneficial for good adhesion, the relevant factor is that the energy of absorption should be large, and this energy may in some cases well be higher for a "contaminated" than for a "clean" substrate surface(ref.8). Clearly in this highly empirical branch of thin film technology the effects of certain procedures will frequently depend on the particular film-substrate combination in question.

On the other hand the increase in film adhesion through irradiation during or after vapour deposition, in the manner we have described, is not restricted to the special case of Germanium films on glass, since the same effect has been observed when either a single crystal of NaCl or well polished polycrystalline Copper was substituted as a substrate material. We are thus led to believe that stronger film bonding will quite generally be obtained through the creation of a transition layer at the substrate boundary.

From considerations of the ion range it was concluded that at the low ion energy used in the present work the formation of such an intermediate layer should only be possible, if the additional kinetic energy required was transferred from the beam to the Germanium atoms within a few Å of the interface. Certain aspects of the experimental evidence were in agreement with this view. In apparent contradiction however it was found that bonding, though strongly enhanced by irradiation of an initial layer of only 50 Å, was nevertheless improved even further, if the layer thickness was increased somewhat. This was so notwithstanding the fact that we were here concerned with films exceeding in nominal thickness the mean ion range. These films would however also probably still have been in the nucleation-growth stage, with only ions impinging on nucleation islands being effective. As observed, adhesion should then become more strongly enhanced as the island density rises with increasing film thickness.

There are indications that the ion dose required for adhesion enhancement is well below that employed in the present experiments, where this, as well as the beam energy, were adjusted largely to suit experimental convenience. The effect of these two factors, as well as that of other deposition parameters, on the film properties, in particular on adhesion and intrinsic stress, is now being investigated, and will be reported in due course.

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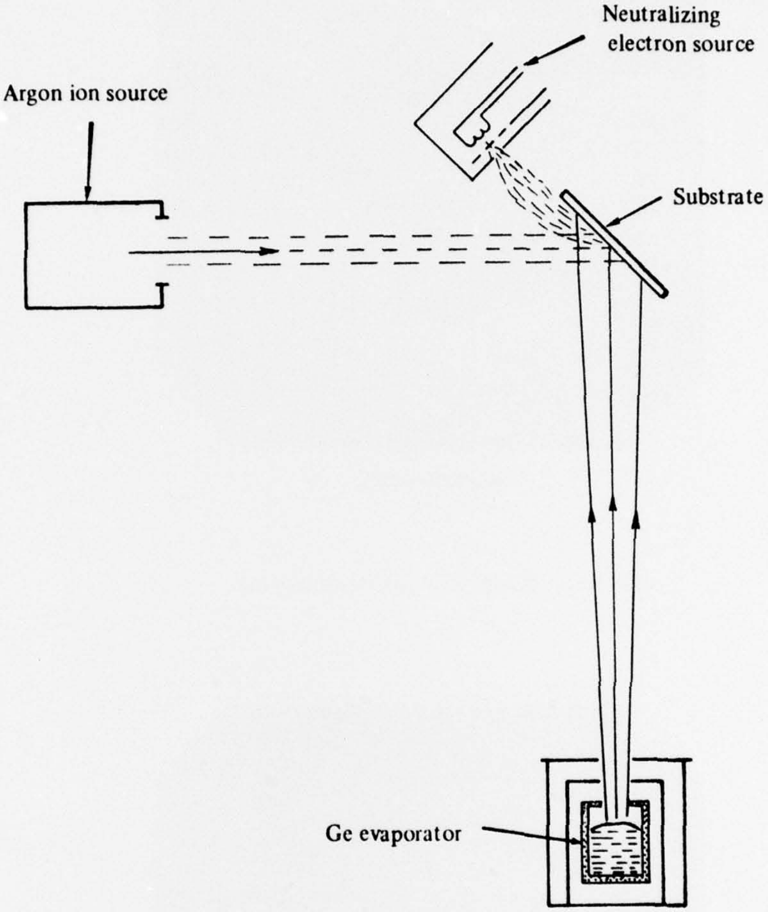

Figure 1. Experimental arrangement (schematic)

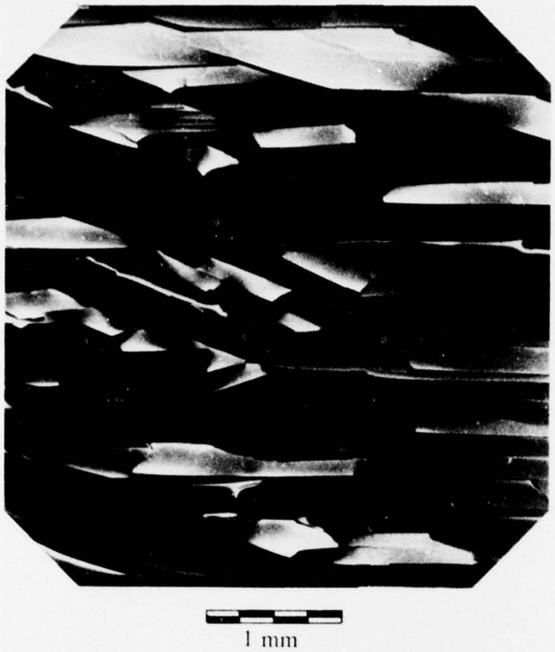

Figure 2. Non-irradiated Germanium film

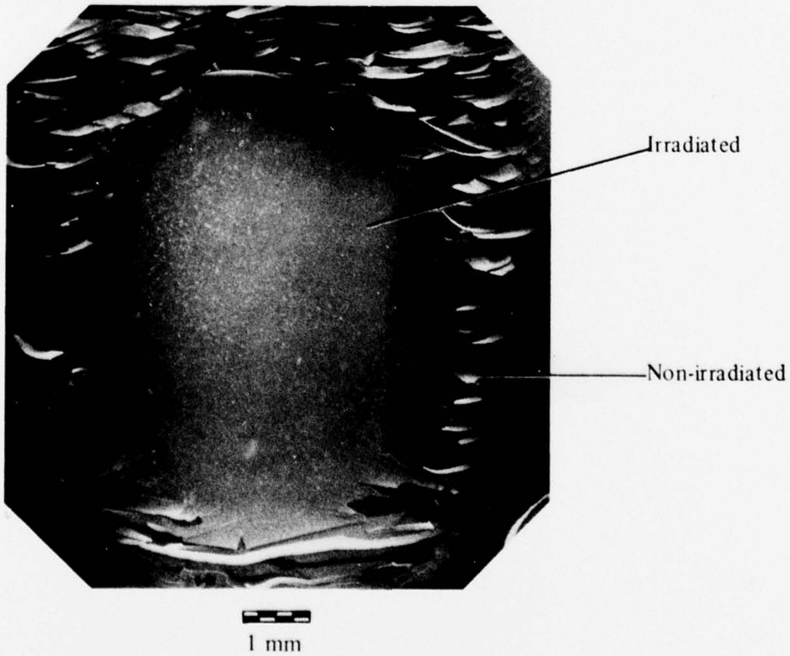

Figure 3. Irradiated Germanium film

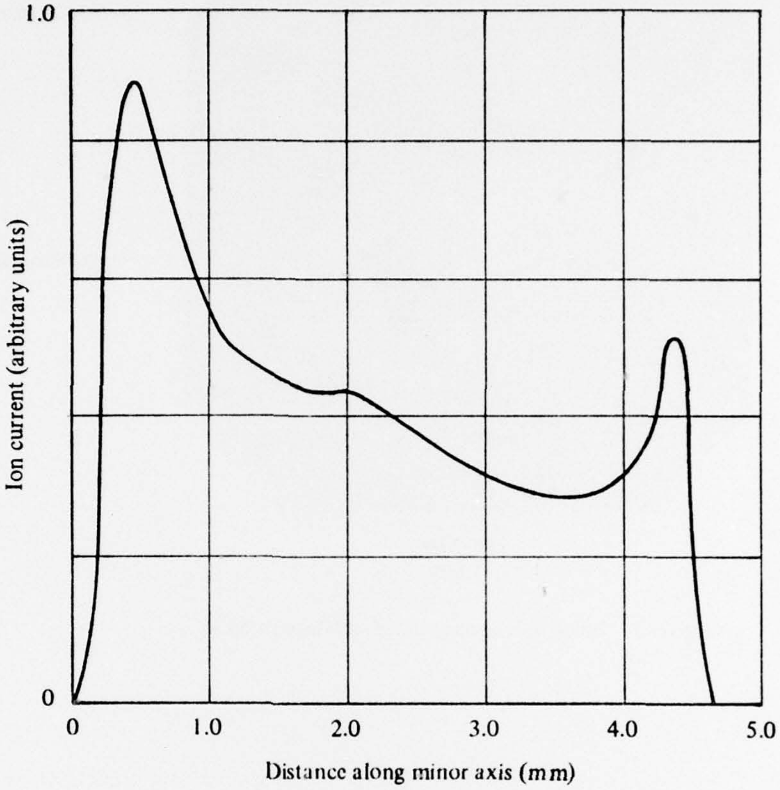

Figure 4. Variation of ion current density along minor axis of the irradiated region

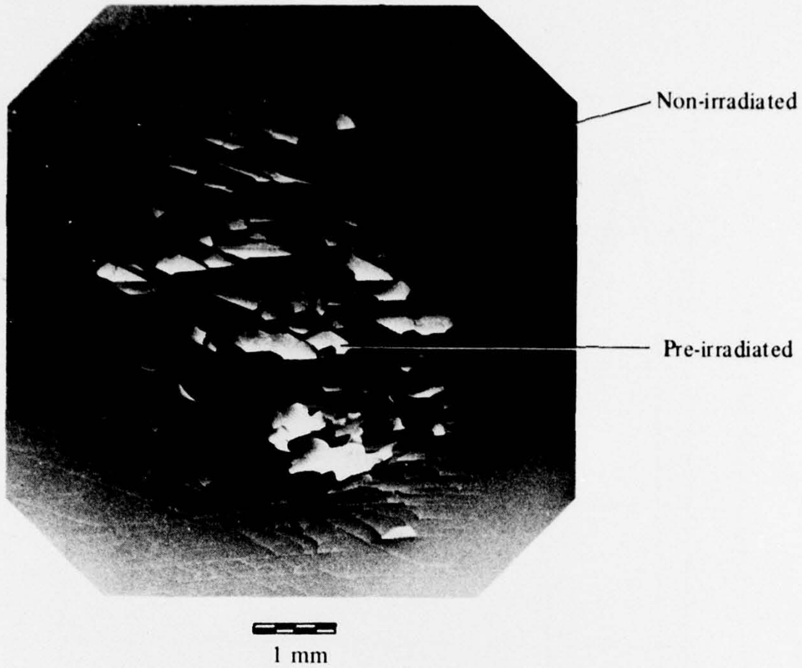

Figure 5. Effect of pre-irradiation on film adhesion

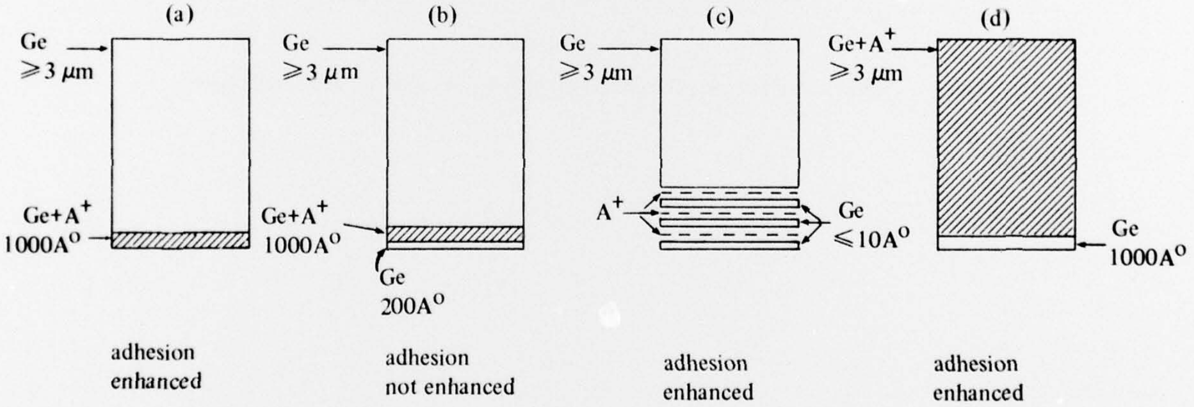

Figure 6. Schematic representation of experimental deposition sequences

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