chemical shifts and quadrupole splittings observed would be consistent with the freezing-in of a metastable high temperature environment as the glass solidifies. Similar results are observed with tin II borate glasses [14].

Although several different starting ratios are investigated in the SnO–GeO_2 system, only three products were produced. The major phases in these products all display the properties of glasses. They all contain distorted Sn (II) electronic environments. The transparent glasses have large refractive indices similar to those found in the PbO–GeO_2 system and higher than those found for all other two-component oxide glasses [3].

Although the SnO must disproportionate during the formation of these materials, the results of this investigation infer that as it is intimately mixed with the GeO_2, it reacts as it disproportionates. Only in the case of $Sn_5Ge_3O_{11}$ was metallic tin apparent. SnO_2 appears to be rejected from the system and was always found on top of the glasses.

References

1. E. M. LEVIN, C. R. ROBBINS and H. F. McMURDIE, "Phase Diagrams for Ceramists" (and supplement) (The American Ceramic Society, Columbus, Ohio, 1964, 1969).
2. J. D. DONALDSON and W. MOSER, *J. Chem. Soc.* (1961) 835.
3. B. PHILIPS and M. G. SCROGER, *J. Amer. Ceram. Soc.* 48 (1965) 98.
4. J. M. FLORENCE, F. W. GLAZE and M. H. BLACK, *J. Res. Nat. Bur. Stand.* **55** (1955) 231.
5. L. MERKER and H. WONDRATSCHEK, *Glastech Ber.* **30** (1957) 471.
6. E. I. SPERANSKOYA, *Izvest. Acad Nauk SSSR, Otdel, Khin Nauk* (1959) 162.
7. G. EULENBERGER, A. WITTMAN and H. NOVOTNY, *Monatsh* 93 (1962) 1046.
8. J. A. TOPPING, I. T. HARROWER and M. K. MURTHY, *J. Amer. Ceram. Soc.* **57** (1974) 209.
9. J. A. TOPPING and M. K. MURTHY, *J. Amer. Ceram. Soc.* **57** (1974) 281.
10. M. I. KAY, R. E. NEWMAN and R. W. WOLFE, *Ferroelectrics* 9 (1975) 1, and quoted references.
11. K. SUGII, S. MIYAZAWA and H. IWASAKI, *Denki Tsushin Kenkyujo Kenkyu Sitsyoka Hokoku* **21** (1972) 359.
12. T. E. CRANSHAW, *Nucl. Instrum. and Methods* **30** (1964) 101.
13. S. R. A. BIRD, J. D. DONALDSON, S. A. KEPPIE and M. F. LAPPERT, *J. Chem. Soc. A* (1971) 1311.
14. J. D. DONALDSON, M. T. DONOGHUE, A. PAUL and M. J. K. THOMAS, unpublished work.

Received 31 August
and accepted 4 October 1976

J. SILVER
E. A. D. WHITE
Department of Electrical Engineering,
Imperial College,
London, UK
J. D. DONALDSON
Department of Chemistry,
Chelsea College,
London, UK

Recoil implantation of materials

In many applications of ion implantation, a shallow (few atomic layers) implant is needed in order to modify the physical and/or chemical properties of the surfaces of materials. An alternative process to conventional ion implantation is recoil implantation which requires less expensive equipment and is possibly more readily adaptable to different material combinations.

In early work of Stroud and co-workers [1–3] a thin film of dopant material was bombarded by energetic argon ions. A fraction of the dopant atoms was recoil implanted into the substrate surface (forward sputtered) and the remainder was sputtered away. Obviously, the forward sputtering yield depends upon the film thickness for given bombarding ion energies and dopant, bombarding and substrate material combinations.

The method proposed is based on maintaining a constant optimal film thickness during the process. A layer which is too thick would effectively shield the interface region, whereas, for a very thin film, the probability of collision between a bombarding ion and a dopant atom would decrease. A continuous deposition of dopant material occurs during the bombardment which just compensates for the loss by resputtering.

The apparatus comprises two adjacent, separately pumped, vacuum chambers, connected by a small aperture. In the higher pressure chamber ($\sim 10^{-3}$ Torr) there is a magnetically confined thermionic argon discharge and a target plate, made of the dopant material and biased to approxi-

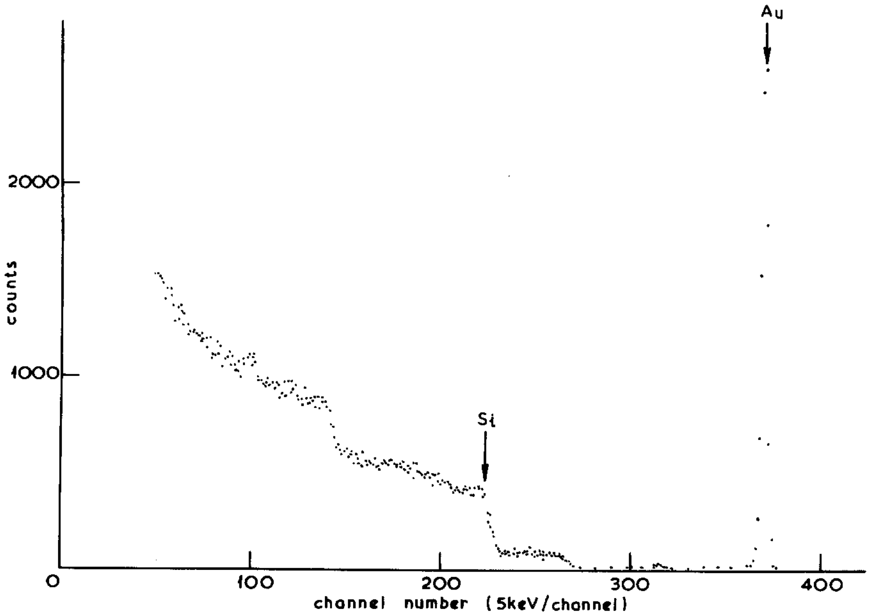

Figure 1 Recoil implanted gold.

mately −1 kV. Owing to the bombardment by positive argon ions from the discharge, sputtering of the target occurs and some of the sputtered atoms of the target material pass through the aperture into the low pressure chamber where they form a deposit on a substrate. Simultaneously, ions can be extracted from the plasma, focused, deflected by a lens and deflector system and accelerated towards the substrate by a high negative substrate potential. This ion beam bombards the deposit of dopant material.

It is expected that any material can be recoil implanted into any substrate. Successful experiments have been carried out with gold and copper using glass substrates. After the treatment and the chemical removal of the remaining deposit from the surface the samples have been analysed by Rutherford back-scattering, which indicated the presence of the dopant under the surface (see Fig. 1). No conclusive results were obtained relating to the precise depth of the implant, but it is anticipated that it was less than about 50 Å.

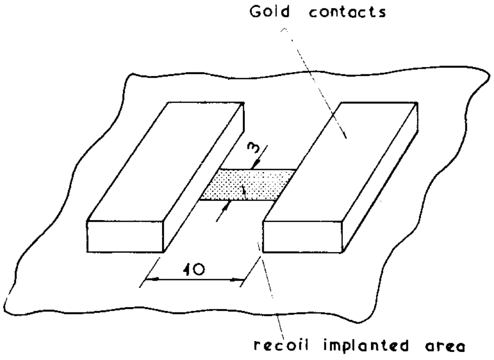

Figure 2 Sample configuration for resistivity measurement.

Samples containing gold with a geometry shown in Fig. 2 have been found to exhibit resistive properties, a value of $6 \times 10^{10}\ \Omega$ being measured, with a linear *V–A* characteristic in the range of 0 to 50 V.

The process of recoil implantation and methods of analysing results are now being further investigated and will be the subject of a future publication.

Acknowledgement

The authors would like to acknowledge the SRC for financial support.

References

1. J. G. PERKINS and P. T. STROUD, AWRE Report No. 09/70 (January 1970).
2. P. T. STROUD, J. G. PERKINS, L. E. COLLINS and K. G. STEPHENS, Nuclear Res. Note 14/71 SSNR AWRE (April 1971).
3. J. G. PERKINS and P. T. STROUD, *Nuclear Instrum. and Methods* **102** (1972) 109.

*Received 9 September
and accepted 4 October 1976*

J. S. COLLIGON
G. FISCHER
M. H. PATEL
*Department of Electrical Engineering,
University of Salford,
Lancs, UK*

Fracture energy of plain and glass-reinforced gypsum plaster

Recent work from this laboratory [1, 2] has clearly demonstrated that addition of a small amount of glass fibre to gypsum plaster converts this essentially brittle material into a quasi-ductile one. This is manifested in the high impact strength of the composite, which is far superior to that of the unreinforced plaster if measured by the pendulum (Izod or Charpy) or the dropping weight methods. Several applications where this improved toughness of glass-reinforced gypsum (grg) can be gainfully utilized have already been suggested [3]. The tests mentioned above, however, do not offer any insight into the processes attending impact failures and for obtaining such information it is sometimes rewarding to consider an approach based on fracture mechanics. For brittle matrix composites such as those based on ceramics, cements or glass, such fracture mechanics studies have already produced some useful results [4–6]. In the present work, similar information has been gathered for gypsum plaster and grg by determining the critical strain energy release rates (G_{IC}) for these materials and their average surface work of fracture (γ_F). γ_F, defined here as the work done to create unit area of new fracture face not taking into account fine scale irregularities in the fracture face, was measured following the techniques developed by Nakayama [7] and Tattersall and Tappin [8]. Phillips [6] has recently discussed the relevance of these measurements for brittle matrix composites.

The gypsum plaster used was fine casting plaster supplied by a UK manufacturer and conforming to BS 1191, Part 1, Class A category. A retarder was added to the plaster at the time of the preparation of the slurry. Slurries having water/plaster ratios (W/P) in the range 0.5 to 0.33 were poured into moulds and after the material had hardened, it was demoulded and test specimens cut from it. The lowest W/P ratio was obtained by removing the excess water by applying suction to the base of the mould.

Glass fibre-reinforced gypsum (grg) was prepared by the spray-suction technique developed at BRE [1, 3]. In this method, glass-fibre strands chopped to suitable lengths assume a random two-dimensional distribution in the plane of the mould. In the present work, the grg boards contained approximately 5 vol% of 32 mm long glass fibres. The glass-fibre strands consisted of 204 filaments of 9.5 μm diameter. Plaster from the same batch used in the manufacture of grg was also cast into moulds at the same time to provide control specimens. The W/P ratio of the "wet" board after suction was 0.33.

In addition to the parameters G_{IC} and γ_F, the bending and impact strength of both plain and reinforced plaster were also determined. For all tests, specimens were cut in the form of rectangular beams of nominal cross-section 10 mm × 17 mm and length 130 mm. One batch of specimens had a larger cross-sectional area, 18 mm × 17 mm. Charpy impact tests were carried out with specimens 75 mm long.

In some of the beams cracks were simulated by cutting central slits with a fine saw, 0.2 mm thick. In some cases the tip of the saw-cut was sharpened with a razor blade. For plain plaster, crack length to beam depth ratios, c/d, were varied initially in the range 0.1 to 0.8, to examine the validity of the fracture mechanics approach in this particular case. For later specimens, prepared with different W/P ratios, only one c/d (0.48) was used. Notched grg specimens were prepared with a c/d ratio of 0.43.