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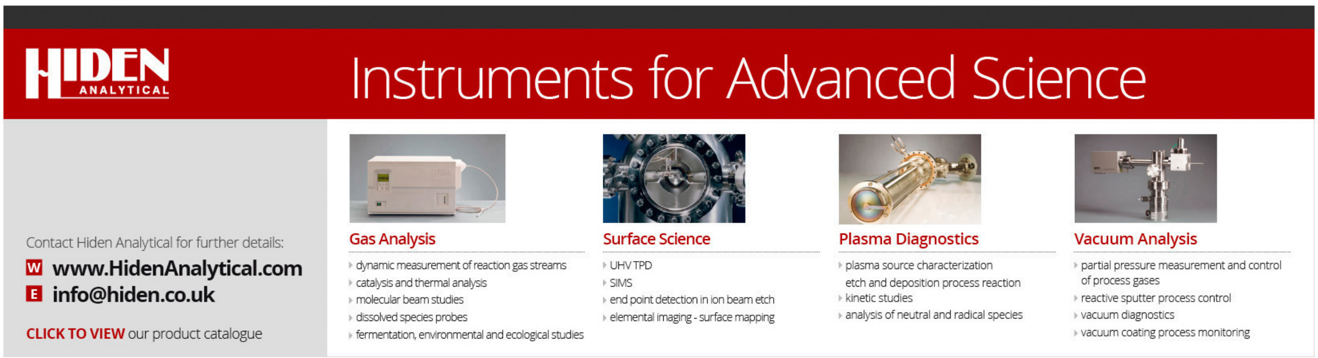

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Estimation of indium-to-germanium and gallium-to-germanium sputtering yield ratios using cosputtering deposition

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The relative concentration of In and Ga atoms incorporated to hydrogenated amorphous germanium (a-Ge:H) films by the cosputtering of solid In and Ga sources together with a crystalline Ge target in a H-containing Ar plasma has been measured by means of Rutherford backscattering spectrometry and particle-induced x-ray emission. Both the experimental In-to-Ge and Ga-to-Ge relative concentrations were found to linearly scale with the respective In/Ge and Ga/Ge sputtered area ratios. From the slopes of these linear dependencies, In-to-Ge and Ga-to-Ge sputtering yield ratios were estimated. The results were found to be consistent with published theoretical sputtering yield values, but to disagree with experimental sputtering yield results previously reported for the case of the In-to-Ge yield ratio. For the case of Ga, a sputtering yield value of 1.6 atoms/ion was deduced from the present results, which gives first experimental account of Ga sputtering by Ar ions.

Sputtering deposition is one of the common methods used for the growth of hydrogenated amorphous silicon[1] (a-Si:H) and germanium[2] (a-Ge:H) of high electronic quality. One of the advantages of this method over the alternative plasma technique of glow discharge is its ability to uncouple the source materials H_2 and Si or H_2 and Ge. In sputtering deposition,[3] solid targets of the materials to be deposited are usually sputtered in a plasma of an inert gas and hydrogen. The use of solid sources constitutes another advantage of sputtering deposition, since these are the usually nontoxic and easier to handle as compared to the gaseous sources used in glow discharge deposition. The above advantages also extend for the purposes of *in situ* semiconductor doping. A great variety of possible solid dopant elements is available, which can be incorporated to the growing film by their cosputtering with the target of the host element. The relative dopant-to-host atomic concentration (N_D/N_H) in a film deposited by cosputtering can be estimated from the dopant-to-host sputtered area (A_D/A_H) and sputtering yield (Y_D/Y_H) ratios, according to $N_D/N_H=(A_D/A_H)(Y_D/Y_H)$. However, for many elements which are potential dopants in both a-Si:H and a-Ge:H, experimental data on sputtering yields are not available in the literature.

In and Ga have been recently shown to act as effective p-type dopants when incorporated into a-Ge:H.[4] While for Ge targets experimental sputtering yield values for various incident ions and energies have been reported in the literature,[5–7] the data available for In and Ga are very limited.[8] In this work, we have measured the amount of In or Ga atoms which incorporate into the a-Ge:H network by the cosputtering of solid In and Ga together with a crystalline Ge target in a H-containing Ar plasma. The resulting In-to-Ge relative atomic concentrations in the films were measured by means of Rutherford backscattering spectroscopy (RBS). For the case of Ga in a-Ge:H, which is troublesome due to the proximity of Ga and Ge in the Periodic Table, proton-induced x-ray emission (PIXE) measurements were used for the determination of the Ga-to-Ge relative atomic concentration. A linear relation between the relative atomic concentrations measured and the sputtered areas was found, which allows us to estimate In-to-Ge and Ga-to-Ge sputtering yield ratios. To the best of our knowledge, the present study gives first experimental account of Ga sputtering yield by Ar ions.

The samples used in the present study were prepared in a conventional rf (13.56 MHz sputtering system in an Ar (99.997%) plus H_2 (99.9995%) atmosphere. A 3 in. diam, water-cooled, crystalline Ge (99.9995%) target was used. The residual pressure of the chamber was 1×10^{-6} mbar. Hydrogen and argon partial pressures were 1.5×10^{-3} and 14.7×10^{-3} mbar, respectively. Rectangular 2×1 cm 7059 Corning glass and crystalline Si substrates were mounted on a grounded substrate holder at a distance of 4.5 cm from the target and held at 220 °C during deposition. The target self-bias potential was -640 V. The a-Ge:H films were deposited at a rate of 1.3 Å/s. The concentration of bonded hydrogen in the films was 5.5 ± 0.5 at. %, as determined from the integrated absorption of the Ge–H wagging vibration mode[9] at 565 cm^{-1}. For the deposition of samples containing In and Ga, the Ge target was partially covered by small pieces of solid In or Ga of varied sizes. The In and Ga pieces exhibited a spherical shape after the deposition run, indicating that melting of the pieces had occurred, though the sputtered electrode was water cooled. The In and Ga specimens were therefore placed in small, high-purity, Ge receptacles and were presputtered during 30 min before each deposition. This procedure was performed in order to produce clean and well-defined In and Ga sputtered areas. The exposed areas of the metallic pieces were measured with an optical microscope immediately after each deposition run. The In-to-Ge relative concentration in the samples was evaluated by RBS measurements using 2 MeV and 2.84 MeV He^+ beams, at 170° scattering angle. The relative Ga atomic concentration

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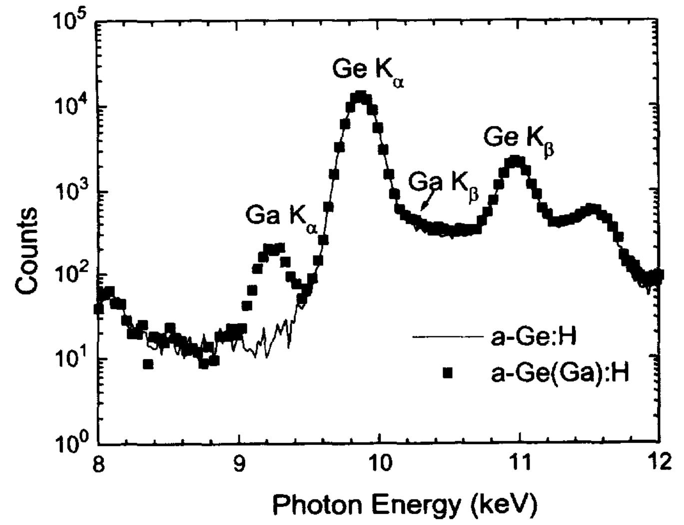

FIG. 1. Typical PIXE spectra induced by 2.4 MeV H^+ incident on undoped (line) and Ga-doped (symbols) *a*-Ge:H films.

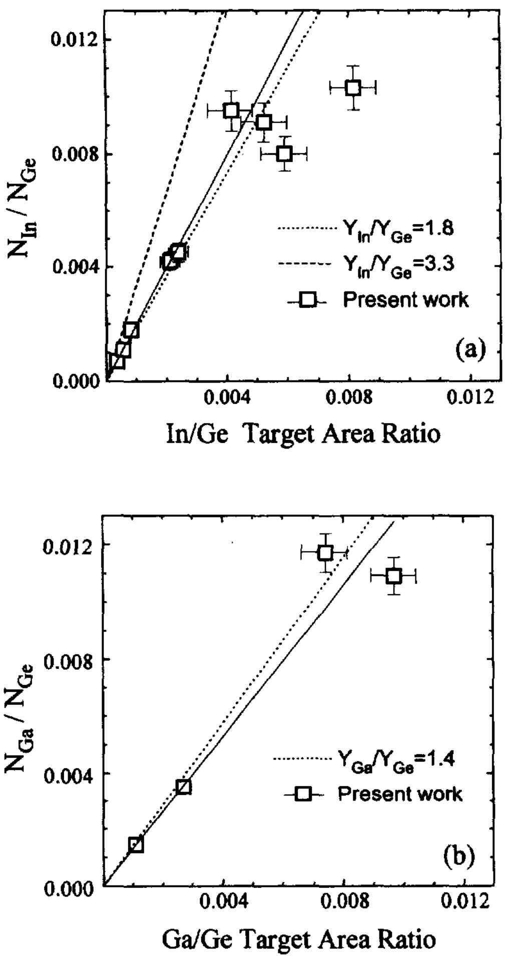

FIG. 2. Relative In-to-Ge (a) and Ga-to-Ge (b) atomic concentrations (N_{In}/N_{Ge} and N_{Ga}/N_{Ge}) as function of the respective relative target sputtered area ratios, as determined by RBS [symbols in (a)] and PIXE [symbols in (b)]. The solid lines are linear fits to the data points, the dotted lines are values estimated using the theoretical sputtering yields from Ref. 14. The dashed line in (a) represents values estimated using experimental Ge and In sputtering yields for Ar ions reported in Refs. 5, 6, and 8.

was determined from PIXE measurements, using a 2.4 MeV H^+ beam and a Si(Li) detector (147 eV resolution) placed at an angle of 135° with respect to the beam. Both PIXE and RBS measurements were performed at the Laboratório de Análise de Materials com Feixes Iônicos (LAMFI-USP).

The In-to-Ge concentrations for the In-doped *a*-Ge:H films were determined from the heights of the In and Ge edges in the RBS spectra[10] and confirmed by using the RUMP code.[11] Figure 1 shows a typical PIXE spectrum obtained for a Ga-doped *a*-Ge:H sample. The interpretation of the present PIXE spectra requires a careful evaluation of the background signal below the Ga $K\alpha$ peak, which is essentially due to the tail of the neighboring Ge $K\alpha$ peak. In the present work, the background signal was determined experimentally by measuring PIXE spectra for various undoped *a*-Ge:H samples deposited under identical conditions (also shown in Fig. 1). Possible fluorescence effects of the Ge $K\beta$ x rays on the intensity of the Ga $K\alpha$ peak were examined by comparing the PIXE spectrum for a thin (44 μg/cm^2) GaP film placed in front of an undoped *a*-Ge:H sample to that obtained for the single GaP film. The area below the Ga $K\alpha$ peak for the composite GaP+Ge target was found to be larger by only 1% than that obtained for the single GaP film. Since the GaP film is transparent to both the H^+ beam and the Ge K x rays, the result above indicates that fluorescence effects are small, and were therefore neglected in the analysis of PIXE spectra. The Ga-to-Ge relative atomic concentration was determined from the ratio of the net areas below the Ga and Ge $K\alpha$ peaks, taking into account differences in ionization cross sections and response of the PIXE detection system. Differences in the Ga and Ge $K\alpha$ x-ray self-absorption in the film were considered[12] and found to be lower than 2%. This is expected due to the similarity between the Ga and Ge binding energies of the K-shell electrons.

Figures 2(a) and 2(b) show the relative In and Ga concentrations (N_{In}/N_{Ge} and N_{Ga}/N_{Ge}) as a function of the In/Ge and Ga/Ge sputtered target area ratios, respectively. It can be seen that, at least for In or Ga concentrations lower than approximately 1×10^{-2}, N_{In}/N_{Ge} and N_{Ga}/N_{Ge} show a linear dependence on the respective sputtered area ratio. This fact would suggest that the dopant incorporation process can be described by simple concepts of physical sputtering, i.e., that the processes which are possible during sputtering deposition,[13] such as reactive etching of the growing film substrate and targets, or resputtering of deposited species from the film surface, have small or negligible influence in the cases studied here. Under this assumption, it is possible to estimate the In-to-Ge and Ga-to-Ge sputtering yield ratios from the slope of straight line fits to the data, which are also shown in Figs. 2(a) and 2(b). The Y_{In}/Y_{Ge} and Y_{Ga}/Y_{Ge} values obtained this way are listed in Table I, together with sputtering yield values and ratios obtained from the literature for 1 keV Ar ions. The experimental Y values were extracted from the compilations in Refs. 5, 6, and 8, while the theoretical sputtering yield values are due to Seah.[14] It can be seen in Table I that both the Y_{In}/Y_{Ge} and Y_{Ga}/Y_{Ge} values deduced in the present work are in very good agreement with the corresponding theoretical ratios. On the other hand, the

TABLE I. Sputtering yield values in atoms/ion reported in the literature for 1 keV Ar ions incident on Ge, In, and Ga, and the corresponding sputtering yield ratios. The entries in the column labeled "present work" correspond to the slopes of linear fits to the data points in Figs. 2(a) and 2(b).

Sputtering yield	Experimental (atoms/ion)	Theory[a] (atoms/ion)	
$Y_{\rm Ge}$	1.5[b]	2.4	
$Y_{\rm In}$	5.0[c]	4.4	
$Y_{\rm Ga}$	···	3.4	
Sputt. yield ratio			Present work
$Y_{\rm In}/Y_{\rm Ge}$	3.3	1.8	2.0
$Y_{\rm Ga}/Y_{\rm Ge}$	···	1.4	1.3

[a] Reference 13.

[b] Value averaged over data in Refs. 5 and 6.

[c] Reference 8.

$Y_{\rm In}/Y_{\rm Ge}$ value as deduced from the experimental sputtering yields in Refs. 5, 6, and 8 is in clear disagreement with (by more than 60%) the corresponding result obtained in the present study. To the best of our knowledge, no experimental results for $\rm Ar^+$ sputtering of Ga have been reported in the literature. One possible source of discrepancy between the presently deduced $Y_{\rm In}/Y_{\rm Ge}$ value and that obtained from the literature could be due to the fact that the In specimens melted during the plasma deposition. The effect of melting on the sputtering yield has been reported for the case of Sn.[15] For Ar ions with kinetic energies between 400 and 800 eV, the sputtering yields for liquid Sn were found to differ from the corresponding values obtained for the solid target by up to 15%.

The fact that both $Y_{\rm In}/Y_{\rm Ge}$ and $Y_{\rm Ga}/Y_{\rm Ge}$ values agree with those calculated from the theoretical sputtering yields by Seah[14] suggests that the target dependence of the sputtering yield as described by the theory gives good account of the relative sputtering rates for the experimental conditions used in the present study. However, it does not imply that the corresponding absolute sputtering yield values are necessarily correct. By comparing the available experimental data on pure element sputtering yields for Ar ions to the values predicted by Sigmund's theory,[16] Seah concluded that experimental results were affected by surface contamination, and developed a correction to the theoretical expression based on the experimental sputtering yield values corrected for contamination effects.[14] For the particular case studied here, it is interesting to note in Table I that the theoretical and experimental sputtering yields for In agree to within 15%, which is of the order of the expected experimental uncertainty, while for the case of Ge the theoretical sputtering yield value disagree with the experimental one by about 50%. Since the sputtering yield for Ge has been measured by different authors with different experimental systems and values differing by less than 10% were found,[5,6] the validity of the theoretical treatment for the prediction of absolute sputtering yields is not warranted. If the experimental sputtering yield value for Ge is taken as a reference,[17] the sputtering yield for ~600 eV Ar ions incident on Ga can be estimated from the $Y_{\rm Ga}/Y_{\rm Ge}$ value found in the present work to be $Y_{\rm Ga}\sim 1.6$ atoms/ion. This result is a first experimental, though indirect, sputtering yield value reported for Ga sputtered by $\rm Ar^+$.

In summary, the relative concentration of In and Ga atoms incorporated to a-Ge:H by the cosputtering of solid In and Ga solid sources together with a crystalline Ge target in a H-containing Ar plasma has been measured by means of RBS and PIXE. It was found that (1) the experimental data can be accurately predicted for relative concentrations lower than approximately 1×10^{-2} according to $N_D/N_{\rm Ge}=(A_D/A_{\rm Ge})(Y_D/Y_{\rm Ge})$, where $Y_D/Y_{\rm Ge}$ equals 2.0 for In-doped a-Ge:H and 1.3 for the case of the Ga-doped films; (2) the $Y_D/Y_{\rm Ge}$ values found in the present work are in good agreement with the sputtering yield ratios calculated from theoretical yield values;[14] and (3) the Ga sputtering yield of $Y_{\rm Ga}\sim 1.6$ atoms/ion for ~600 eV Ar ions has been estimated from the present experimental results and the measured Ge sputtering yield values reported in the literature.

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