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Structure and composition of amorphous $\text{Ge}_{1-x}\text{Sn}_x$ thin films

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The composition and bonding configuration of amorphous germanium-tin ($\alpha\text{-Ge}_{1-x}\text{Sn}_x$) thin films are reported ($0 \leq x < 0.3$). Mössbauer spectroscopy analyses show that under the reported deposition conditions all tin atoms enter the $\alpha\text{-Ge}$ network in a perfect substitutional way, i.e., in a covalent tetrahedral configuration. The absence of defect structures in the tin sites is discussed and compared with results on films prepared under different conditions.

The science and technology of amorphous alloys have been very active fields over the past years. In particular, for solar cells and optical sensors, materials with variable band gaps are highly desirable.¹ Major advances occurred in the understanding of the gross features of the electronic band structures of $\alpha\text{-Si}$ and $\alpha\text{-Ge}$ alloys and variations in the optical band gap could easily be obtained. The low-band-gap amorphous semiconductors, e.g., Si- (or Ge-) Sn alloys, deserved up to now much less attention than the higher-band-gap materials. The present work deals with the composition and bonding structure of $\alpha\text{-Ge}_{1-x}\text{Sn}_x$ thin films prepared by rf sputtering. The subject was addressed more than a decade ago by Temkin and co-workers.^{2,3} These studies on alloy composition and crystallization temperature established the following: (a) Amorphous $\text{Ge}_{1-x}\text{Sn}_x$ films prepared at low temperatures (-10°C) have a random tetrahedral bonding, the relative ratio of Ge-Sn bonds to Ge-Ge bonds (and to Sn-Sn bonds) being around 2:1 in the $x = 0.5$ composition. (b) The quenching of $\alpha\text{-Ge}_{1-x}\text{Sn}_x$ samples from near the crystallization temperature produces a two-phase film: crystalline $\text{Ge}_{1-y}\text{Sn}_y$ and $\beta\text{-Sn}$ with $y < x$ and no evidence of amorphous $\text{Ge}_{1-x}\text{Sn}_x$.

The films of the present work were deposited at higher substrate temperatures ($T_s = 180^\circ\text{C}$) and cooled down at much slower rates. New and unique features appeared concerning the bonding structure and the composition of the films. Solid solutions of Ge and Sn are obtained for tin concentrations up to 27 at. %, as deduced by conversion-electron Mössbauer spectroscopy (CEMS) and Rutherford backscattering spectrometry (RBS) techniques. No structures of defects (vacancies, dangling bonds, voids, etc.) were detected around the Sn sites, indicating that in the materials of the present work all tin atoms are covalent and tetrahedrally bonded.

Amorphous Ge and $\text{Ge}_{1-x}\text{Sn}_x$ films were deposited by rf sputtering in a Leybold-Heraeus Z-400 apparatus. The target was a 2-in.-diam, 1/4-in.-thick, 99.999% pure Ge disk upon which small pieces of 99.999% pure Sn were placed in an approximately random way to prepare alloy films. The system was dry pumped prior to deposition to a base pressure of 10^{-6} mbar during 1 h. The argon gas was of 99.9995 at. % nominal purity. Four series of samples were prepared under identical deposition conditions with the exception of the Sn target coverage. The tin content of the alloy varied between 0 and around 30 at. %. The substrates, high-purity

crystalline silicon and Corning 7059 glass were ultrasonically precleaned and kept at 180°C during the deposition. The target was plasma etched for several minutes before each run began. The total pressure was 1.5×10^{-2} mbar in all cases. The rf power was adjusted in each series in order to give a deposition rate of 1 \AA s^{-1} . Typical sample thickness was $1 \mu\text{m}$.

The Ge and $\text{Ge}_{1-x}\text{Sn}_x$ thin-film samples were characterized by means of RBS and CEMS. The RBS analyses were performed with a 760-keV $^4\text{He}^{2+}$ beam from the Porto Alegre HVE-400 ion implanter. The overall resolution of the RBS spectrometer was 14 keV.

The CEMS spectra were obtained in a backscattering geometry by mounting the samples on the backplate of a proportional counter through which $\text{He} + 5\% \text{CH}_4$ was allowed to flow. Measurements were taken with the sample and source at room temperature. A conventional constant acceleration Mössbauer spectrometer was used. Further details on the technique can be obtained from Refs. 4-6. The Mössbauer source used was $^{119\text{m}}\text{Sn}$ in BaSnO_3 . The isomer shifts are quoted with respect to this source.

In Fig. 1 we show the RBS spectra of an $\alpha\text{-Ge}$ sample

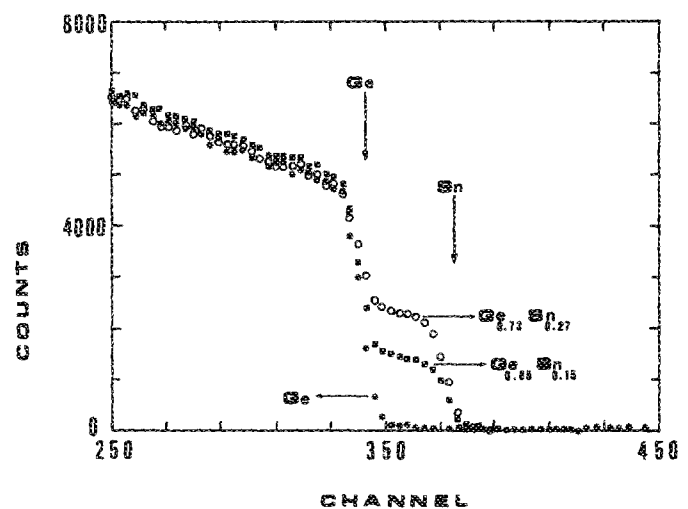


FIG. 1. Rutherford backscattering spectra from the sputtered $\alpha\text{-Ge}$, $\alpha\text{-Ge}_{0.85}\text{Sn}_{0.15}$, and $\alpha\text{-Ge}_{0.73}\text{Sn}_{0.27}$ thin-film samples deposited on Corning 7059 glass substrates. Incident α -particle beam energy, 760 keV; resolution of the spectrometer, 14 keV. The vertical arrows indicate the positions in the RBS spectra of surface Sn and Ge.

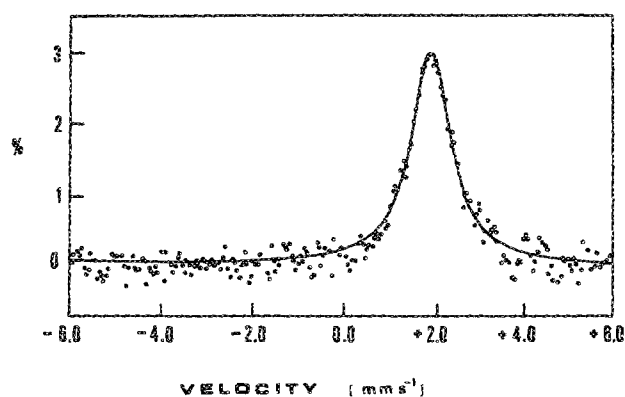


FIG. 2. ^{119}Sn conversion-electron Mössbauer spectrum from the sputtered $a\text{-Ge}_{0.73}\text{Sn}_{0.27}$ sample. The solid line represents the least-squares fitting of the experimental points with a single Lorentzian component with isomer shift $\delta = 1.95 \pm 0.06 \text{ mm s}^{-1}$ and linewidth at half maximum $\Gamma = 1.10 \pm 0.08 \text{ mm s}^{-1}$. The source was ^{119m}Sn in BaSnO_3 .

and two $a\text{-Ge}_{1-x}\text{Sn}_x$ films. From the analyses of the relative amplitudes of the Sn and Ge signals, we obtain the values for x in the two alloy samples: $x = 0.15$ and 0.27 , respectively. Within the limits of RBS detection, there is no evidence of any kind of contamination during deposition. Independent analyses with infrared (IR) transmission spectroscopy and Auger electron spectroscopy confirm the absence of oxygen and carbon contamination. Another aspect that appears clearly from the inspection of the RBS spectra is the flatness of the plateaus, an indication that there is no Sn segregation, neither in the outermost surface nor in the interior of the film. This observation was also confirmed by sputtered Auger depth profiling of Sn and Ge.

Figure 2 shows the ^{119}Sn CEMS spectrum corresponding to the sample whose composition, according to the RBS data, is $\text{Ge}_{0.73}\text{Sn}_{0.27}$. The solid line represents the least-squares fitting of the CEMS spectrum with a single Lorentzian line. The Mössbauer parameters extracted from the fitting are $\delta = 1.95 \pm 0.06 \text{ mm s}^{-1}$ for the isomer shift and $\Gamma = 1.10 \pm 0.08 \text{ mm s}^{-1}$ for the linewidth at half maximum. The CEMS spectrum for the sample with composition $\text{Ge}_{0.85}\text{Sn}_{0.15}$ is identical to that shown in Fig. 2. The results being presented here are to be compared with the work of Weyer *et al.*⁷ for ^{119}Sn in crystalline Ge and with the work of Nanver, Weyer, and Deutch⁸ for ^{119}Sn in amorphous germanium. The comparison leads us to conclude that the Mössbauer parameters extracted from the fitting of Fig. 2 correspond to ^{119}Sn in amorphous germanium. It is noteworthy in Fig. 2 that the CEMS spectrum is perfectly fitted with just one singlet, which eliminates the possibility of other components in the spectrum associated with dangling bonds on the Sn tetravalent coordination or other defect structures around the Sn probe.⁹ Other authors have investigated the Ge-Sn system with transmission and reemission Mössbauer spectroscopy.^{7,8,10,11} Their results were always derived from one of the two following situations: (a) Very small Sn concentrations in $c\text{-Ge}$ or $a\text{-Ge}$ (such as $10^{18}\text{--}10^{19} \text{ cm}^{-3}$ ion-implanted ^{119}Sn) produce 100% solid solutions of Sn in Ge after adequate thermal treatments at temperatures above 300°C . However, samples that were not thermally treated

always presented $\beta\text{-Sn}$ precipitates, Sn vacancies, or other defect structures. (b) Higher Sn concentrations, up to those of the present work, always induced $\beta\text{-Sn}$ precipitates and other defect structures that clearly appear in their Mössbauer spectra.

It is interesting to speculate about the possible relationship existing between the findings of the CEMS and the details of infrared transmission data taken on hydrogenated $a\text{-Ge}_{1-x}\text{Sn}_x$ thin films.¹² Films deposited under the same conditions as those reported here, except the presence of controlled amounts of hydrogen in the reaction chamber, were analyzed by IR spectroscopy. The spectra showed in all cases the characteristic absorption bands of the Ge-H (1895-cm^{-1}) and Ge-H₂ (1975-cm^{-1}) stretching modes, as well as the 565-cm^{-1} wagging mode absorption band.¹³ The position of the peaks appears slightly shifted toward low frequencies as the tin content increases in the alloy. However, they unambiguously correspond to the germanium-hydrogen localized vibrational modes. None of the hydrogenated samples show absorption bands that could possibly be attributed to Sn-H vibrations. This experimental observation might be due to an absolute preference of H atoms to bond to Ge instead of to Sn (a tendency of the like has already been reported to exist in $a\text{-Si-Ge}$ alloys where the H atoms prefer to attach to Si orbitals¹⁴).

Summarizing, we have shown the following:

- (1) It is possible to prepare at 180°C stable Ge-Sn amorphous solid solutions with Sn concentrations ranging from 0 up to nearly 30 at. %.
- (2) Under the preparation conditions being reported here, all Sn atoms bond to the $a\text{-Ge}$ network in a covalent-tetrahedral configuration, e.g., in a substitutional way.
- (3) As a consequence, no defect structures (like vacancies, voids, dangling bonds, or metallic precipitates) are detected by Mössbauer spectroscopy in tin sites.

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¹See, for instance, the numerous articles appearing in *Amorphous Semiconductors: Technologies and Devices*, edited by Y. Hamakawa (OHM-North Holland, Tokyo, Japan, 1984).

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Free-carrier density determination in *p*-type GaAs using Raman scattering from coupled plasmon-phonon modes

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A nondestructive optical means of determining the activated hole concentration in *p*-type polar semiconductors is described. The Raman spectra from coupled plasmon-longitudinal-optical-phonon modes in five samples of Be-doped GaAs are measured and fitted using a theory which takes into account the degenerate light- and heavy-hole valence bands. The results indicate that coupled plasmon-longitudinal-optical-phonon modes in *p*-type material differ both quantitatively and qualitatively from those in *n*-type semiconductors.

Nondestructive techniques for determining the activated free-carrier concentration in semiconductors have obvious technological advantages over more traditional, destructive techniques such as the Hall effect and spreading resistance. Optical techniques, including local-mode Raman scattering,¹ infrared reflectivity,² and infrared total internal reflection,³ have been successfully used with group-IV semiconductors for this purpose. In *n*-type polar materials such as GaAs or InP, Raman scattering from the two coupled plasmon-longitudinal-optical (LO)-phonon modes⁴ has proven to be a useful method for determining the free-carrier concentration. The density is obtained by fitting the measured energies of the two modes, ω_- and ω_+ , with calculated values, based on the density-dependent free-carrier contribution to the system's dielectric response function.⁵

To our knowledge, Raman scattering from coupled plasmon-LO-phonon modes has not yet been used to extract activated hole concentrations from *p*-type polar semiconductors. The purpose of this communication is to demonstrate that the free-hole concentration in Be-doped, *p*-type GaAs can in fact be obtained by fitting the Raman spectra from these coupled modes, despite the fact that the nature of these modes is entirely different in *p*-type as opposed to *n*-type material. In addition to providing a useful diagnostic tool, this study reveals three novel features of the coupled modes in *p*-type polar semiconductors: (1) rather than the plasmons coupling with the LO phonons to produce two distinct branches, ω_- and ω_+ as in *n*-type materials, only a single coupled mode is observed in the *p*-type material, (2) the Raman line shapes are quite sensitive to the light-hole population and hence to the extrinsic damping processes involving these carriers, and (3) inter-valence-band (heavy-

and light-hole) transitions provide intrinsic electronic damping of significant strength.

The Raman spectra were obtained using the 532.4-nm output from a cw mode-locked and frequency-doubled yttrium aluminum garnet (YAG) laser, in a near-backscattering geometry. The average power was kept below 250 mW, which was much less than that required to observe intensity-dependent effects on the Raman spectra from the coupled modes. The excitation beam was vertically polarized and the scattered light was horizontally analyzed before entering a triple spectrograph. A liquid-nitrogen-cooled Si charge-coupled-array detector was used to record a 300-cm⁻¹-wide spectrum during a single exposure. All spectra were obtained at 300 K.

Five GaAs samples were grown and doped in a molecular-beam-epitaxy (MBE) machine with Be concentrations varying between 1×10^{18} and 3×10^{19} cm⁻³. Table I serves to identify the samples; the Hall density and Hall mobility, as measured at 300 K, are listed in columns 2 and 3, respec-

TABLE I. Sample characteristics.

Sample	Hall measurements		Raman measurement
	Total hole density (10 ¹⁸ cm ⁻³)	Mobility (cm ² /V s)	Total hole density (10 ¹⁸ cm ⁻³)
a	1.0	175.0	1.5
b	4.5	123.0	3.0
c	6.0	100.0	4.5
d	8.0	120.0	7.0
e	30.0		20.0