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PRESSURE-INDUCED TRANSITIONS IN AMORPHOUS SILICON AND GERMANIUM

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Abstract.- Pressure-induced transitions from semiconductor to metal in a-Si, a-Ge and their alloys have been investigated by measurements of the optical absorption edge, electrical resistivity, superconductivity, X-ray diffraction and Raman scattering as a function of pressure. The transitions, accompanied by discontinuous changes in optical gap and resistivity occur in evaporated a-Si and a-Ge and in silane-decomposed a-Si:H while in reactively sputtered a-Si:H and a-Ge:O they show a continuous decrease in resistivity. It is shown by X-ray diffraction experiments that these transitions are accompanied by a change of structure which is heterogeneous with a mixture of two metastable phases. The metallic modification of a-Si under pressures of 100 to 150 kbar is reversible to the amorphous state after the compression. New metastable polymorphs of hexagonal Ge and tetragonal Si:H are recovered.

Introduction.- High-pressure researches have contributed significantly to our understanding of the properties of condensed matter. The primary effect of pressure is to decrease the interatomic distance. As a consequence, the compression gives rise to a change in electronic structure and a phase transition from semiconductor to metal. For example, the pressure-induced transitions, accompanied by a sharp drop in resistivity by a factor of approximately $10^{-10}$, occur in a-Si at 100 kbar and in a-Ge at 60 kbar whereas in the crystalline state their transition pressures are 150 and 100 kbar respectively [1-4].

Recently the systematic changes in atomic structure and electronic properties of plasma-deposited a-Si:H films with preparation conditions have been extensively investigated because of the technological importance. The electronic properties of these films are very sensitive to the atomic structure and defects which depend on the preparation method. The atomic structure of silane-decomposed a-Si:H films is characteristic of a cross-linked network of Si atoms with SiH bonding [5]. On the other hand, in reactively sputtered films it is typical of a low-dimensional network with a mixture of SiH and SiH$_2$ bonding [6].

The atomic structure and defects in the plasma-deposited a-Si:H films are reflected in the pressure-induced transitions and the associated changes in optical gap and resistivity. Welber and Brodsky reported the pressure-induced shift in the optical absorption edge to lower energy and the hysteresis after the compression for silane-decomposed a-Si:H films [7]. Weinstein reported the pressure-induced shift of the photoluminescence peak to lower energy and the quenching of intensity [8].

It is the purpose of this paper to discuss the experimental results about the effect of pressure on optical absorption edges, resistivities, superconductivities, atomic structures and Raman-active phonon frequencies and the pressure-induced phase transitions in a-Si, a-Ge and their alloys. From X-ray diffraction experiments it is shown that these transitions are accompanied by a change of structure which is heterogeneous with a mixture of two metastable phases. The metallic character of the high-pressure phases is demonstrated by the superconductivity. The associated changes in optical gap and resistivity are discussed with the H environments and defects in plasma-deposited a-Si:H films. The emphasis will be on the difference of transition processes between silane-decomposed and reactively sputtered films.
Pressure Dependence of Absorption Edge.- The effect of pressure on the optical absorption edges has been measured for a-Si:H films prepared by glow-discharge decomposition of pure silane with a RF diode apparatus and by reactive sputtering of Si target in Ar - H\textsubscript{2} gaseous mixture with a RF - DC tetrode apparatus. The optical absorption coefficient $\alpha$ in the fundamental edge region of these plasma-deposited films follows the relation $(\alpha h\nu)^{1/2} = B(h\nu - E_o)$. The optical gap $E_o$ is given from the extrapolation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves [9,10].

The measured absorption edges as a function of pressure are shown in Fig. 1. The absorption edge shifts to lower energy with increasing pressure. The behavior of silane-decomposed and reactively sputtered a-Si:H films is qualitatively similar. The absorption coefficient increases with pressure in the forbidden-gap region. The silane-decomposed films become rapidly opaque at about 130 kbar. However, the reactively sputtered films become gradually opaque under pressures of 150 to 170 kbar [Tsuiji and Minomura].

The variation of optical gap with pressure is shown in Fig. 2. The initial pressure dependence is of order $-1 \times 10^{-3}$ eV/kbar, which is nearly equal to that of the conduction-band minimum at X point with respect to the valence-band maximum in c-Si. The pressure-induced shift in a-Si:H films is accelerated in higher rate above 50 kbar. The optical gap shrinks to zero at the transition to the metallic state. After the compression below the transition point these films show a large hysteresis. It grows larger with increasing the applied pressure.
Transitions from Semiconductor to Metal.- The effect of pressure on resistivities in evaporated a-Si and a-Ge and in plasma-deposited a-Si:H and a-Ge:O has been measured [1,4]. The variation of resistivity with pressure for a-Si and a-Si:H is shown in Fig. 3. The pressure-induced transitions, accompanied by a sharp drop in resistivity over ten orders of magnitude, occur in silane-decomposed a-Si:H films at about 130 kbar. The similar transitions occur in evaporated a-Si at 100 kbar and in c-Si at 150 kbar. On the other hand, reactively sputtered films under pressure become metallic with a continuous decrease in resistivity at about 170 kbar. After the compression these films show a remarkable hysteresis. At the second compression the continuous transitions are repeated.

The variation of resistivity with pressure for a-Ge and a-Ge:O is shown in Fig. 4. The discontinuous transitions occur in evaporated a-Ge films at 60 kbar while in reactively sputtered a-Ge:O films the continuous transitions occur at about 120 kbar.

The metallic character of the high-pressure phases has been demonstrated by the superconductivity [1]. The variation of resistance with temperature at 170 kbar for silane-decomposed a-Si:H and c-Si is shown in Fig. 5. The high-pressure phases of a-Si:H and c-Si become superconducting with a discontinuous change in resistance at 6.8 and 7.4 K respectively [Sakai, Kajiwara, Tsuji and Minomura]. In Fig. 6, the superconducting transition temperatures $T_c$ as a function of pressure are shown with the reported data for group IV elements [11,12]. The pressure dependence of $T_c$ in the crystalline and amorphous state is qualitatively equal. The metallic modifications of a-Si and a-Ge are classed as a hard superconductor with critical magnetic field of 3.3 and 1.7 kG respectively.
High-Pressure Modifications. - The X-ray diffraction patterns for evaporated a-Si and a-Ge as a function of pressure have been obtained [2,3]. The observed intensity profiles of a-Si are shown in Fig. 7. They reveal the growth and development of new crystalline peaks over the amorphous background under pressures of 100 to 120 kbar. Their peaks correspond to the (101) and (211) reflections of white-Sn structure, which can be converted from the (111) and (311) spacings of diamond structure by displacing atoms one-dimensionally. The high-pressure phases of a-Si below 150 kbar is reversible to the amorphous state after the compression. The high-pressure phases above 150 kbar show the additional diffraction peaks which correspond to the (200), (220) and (301) reflections of white-Sn structure. After the compression they show a transformation to a body-centered cubic (BC-8) structure.

The observed intensity profiles of a-Ge are shown in Fig. 8. They reveal the growth of two polymorphs with white-Sn and (BC-8) structure over the amorphous background at 70 kbar. Above 100 kbar the (BC-8) polymorph shows a further change to white-Sn structure. After the compression the high-pressure phases transform to the (BC-8) structure, but in two days it shows a further transformation to hexagonal (6H) structure.

The high-pressure phase of reactively sputtered a-Si:H at 180 kbar transforms to a tetragonal polymorph after the compression [4]. The observed X-ray patterns are shown in Fig. 9. However, the materials stay in the amorphous state after the compression below 150 kbar. These results suggest that the metallic conduction is due to the similar change of structure to evaporated a-Si.
Fig. 7: X-ray diffraction patterns for evaporated a-Si under pressure.

Fig. 8: X-ray diffraction patterns for evaporated a-Ge under pressure.
Pressure Dependence of Raman Spectra.- The effect of pressure on Raman-active phonon frequencies of the TO and TA modes in plasma-deposited a-Si:H films has been measured [Ishidate, Inoue, Tsuji and Minomura]. These films show the first-order Raman spectra of the TO mode at 475 cm\(^{-1}\) and the TA mode at about 150 cm\(^{-1}\) [13]. The measured phonon frequencies as a function of pressure for reactively sputtered films are shown in Fig. 10. The TO phonon frequencies increase with increasing pressure in a rate of \(1.0 \pm 0.2\) cm\(^{-1}\)/kbar. The pressure dependence is twice larger than that of c-Si. The TA phonon frequencies decrease with increasing pressure in a rate of \(0.5 \pm 0.2\) cm\(^{-1}\). The observed spectra show the broadening to lower frequency with pressure.

\[\text{Fig. 9: X-ray diffraction pattern for a-Si:H after the compression at 180 kbar.}\]

\[\text{Fig. 10: Raman-active phonon frequencies as a function of pressure for a-Si:H.}\]
Discussion.- In this paper we have briefly reviewed experimental results of the effect of pressure on optical absorption edge, electrical resistivity, Raman-active phonon frequency and X-ray diffraction patterns and the pressure-induced transitions from semiconductor to metal in evaporated a-Si and a-Ge and plasma-deposited a-Si:H and a-Ge:O. These transitions reflect the atomic structure and defects which depend critically on the preparation conditions.

The X-ray diffraction patterns for the high-pressure phases of evaporated a-Si and a-Ge reveal the growth and development of metastable white-Sn like modifications over the amorphous background as shown in Figs. 7 and 8. These structural phase transformations are obviously heterogeneous with a mixture of two metastable phases. The first and second diffraction peaks of the high-pressure metallic modifications correspond to the (101) and (211) reflections of white-Sn structure respectively. The metallic modifications of a-Si under pressures of 100 to 150 kbar are reversible to the amorphous state after the compression.

It is known that crystalline Si and Ge under pressure become metallic with a change of structure from diamond to white-Sn type [14,15,16]. In the white-Sn type of Si each atom has four first neighbors at 2.430 Å and two second neighbors at 2.585 Å, so the average interatomic distance increases by a factor of $r_G = 1.0925$ while the volume decreases by a factor of $\Delta V a B = -0.209 V_a$. This structural change can be accomplished by displacing atoms along c-axis. From these results it is considered that the metallic conduction in a-Si and a-Ge under pressure arises from the white-Sn like modifications which are extending one-dimensionally across the entire films. Moreover, the bonding nature of these metallic modifications appears to be a mixture of metallic and covalent character [2]. The reversible transitions in a-Si may be due to the higher covalency.

The information on atomic structure and defects in plasma-deposited a-Si:H films has been derived from a variety of measurements. The infrared absorption spectra are identified as four types of bonding conformations, SiH, SiH$_2$, SiH$_3$ and (SiH$_2$)$_n$ complex [5,6,17]. In the films deposited from glow-discharge plasma of silane at high substrate temperatures of 200 to 350°C the H atoms are incorporated as predominantly SiH bonding while in the reactively sputtered films they are formed as a mixture of SiH and SiH$_2$ bonding. The Si radial distribution function shows that the first coordination number decreases to $3.7 \pm 0.1$ with increasing H content in the silane-decomposed films of 7 to 20 at.% H whereas in the reactively sputtered films it decreases more rapidly to $3.3 \pm 0.1$. From these results it is proposed that the SiH environments may be associated with small voids of two-dimensional character and the SiH$_2$ environments may be associated with larger voids of one-dimensional character. In addition, the reactively sputtered films contain Ar atoms of 6 to 8 at.% which may contribute to the decrease in the first coordination number [18].

The silane-decomposed a-Si:H films under pressure become metallic with a sharp drop in resistivity at about 130 kbar. The transition pressure does not change appreciably with H content. The similar transitions occur in evaporated a-Si at about 100 kbar and in evaporated a-Ge at about 60 kbar. On the other hand, the reactively sputtered a-Si:H and a-Ge:O films under pressure become metallic with a continuous decrease in resistivity at about 170 and 120 kbar respectively. These continuous transitions have been observed in lone pair amorphous semiconductors [19,20].

The optical gap of plasma-deposited a-Si:H films decreases to lower energy with increasing pressure and shrinks to zero at the transition point. However, in the reactively sputtered films at about 150 kbar there is large discrepancy between the optical gap and the activation energy for electrical conduction. The films show the optical gap of about 1.0 eV, but their activation energy is below 0.1 eV. It is considered in the two-phase region that the optical gap is determined by the optical absorption in amorphous semiconductors and the activation energy is determined by the electrical conduction in inhomogeneous structural modifications.

The plasma-deposited a-Si:H films show the pressure-induced absorption in the forbidden-gap region. After the compression these films show a hysteresis which grows larger with increasing the applied pressure. These changes are considered to arise from the structural modifications near H atoms.
The plasma-deposited a-Si:H films show the first-order Raman spectra which are denoted as the TO, LO, LA and TA modes [13]. Crystalline Si shows the first-order peak of the O(r) mode at 520 cm\(^{-1}\) and the second-order peaks of the 2TA(X) mode at 302 cm\(^{-1}\) and the 2TA(L) mode at 231 cm\(^{-1}\) [21]. The TO peak of a-Si:H films lies at 475 cm\(^{-1}\) at atmospheric pressure and shifts to higher frequency with increasing pressure. The observed pressure dependence is twice larger than that of c-Si. The disorder-induced peak of the TA mode is observed at about 150 cm\(^{-1}\). This peak shows the broadening to lower frequency with pressure. The TA phonon frequency depends on predominantly the bond-bending or directional force constant \(\kappa\) whereas the LA phonon frequency depends on predominantly the bond-stretching or central force constant \(\alpha\). The softening of the TA mode with pressure is due to the decrease in \(\kappa\) [22].

The high-pressure metallic phases of c-Si and a-Si:H at 170 kbar become superconducting with transition temperatures of 7.4 and 6.8 K respectively. The transition temperature \(T_c\) follows the relation \(T_c = 1.14\langle h\omega \rangle \exp[-(l/NV)]\), where \(\langle h\omega \rangle\) is the mean energy of phonons, \(N\) is the density of state at Fermi surface in the normal state and \(V\) is the electron-phonon interaction parameter [23]. As shown in Fig. 6, the values of \(T_c\) for group IV elements decrease with increasing pressure. The negative pressure dependence is mainly due to the decrease in \(N\). The observed \(T_c\) for the high-pressure phases of c-Si and a-Si:H does not change appreciably. The contribution of H incorporation to \(N\) is expected to be small.

References.

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