PHYSICAL REVIEW B VOLUME 31, NUMBER 4 15 FEBRUARY 1985

Chemical bonding of hydrogen and oxygen in glow-discharge—deposited thin films of *a*-Ge:H and *a*-Ge:(H,O)

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(Received 3 October 1984)

We have grown thin films of *a*-Ge:H and *a*-Ge:(H,O) by the glow-discharge process, and have used infrared (ir) absorption spectroscopy to study the local bonding of hydrogen and oxygen as a function of the substrate temperature T_s and the amount of O_2 and/or H_2O added to the germane gas mixture in the plasma. The temperature dependence of the ir features associated with monohydride and dihydride groups in *a*-Ge:H alloys is different in these films, grown at relatively high plasma power, from what has been reported in films of *a*-Si:H grown from silane plasmas at lower power levels. In particular, dihydride incorporation in these *a*-Ge:H films displays a distinct temperature threshold, rather than a competition with the monohydride bonding as in the *a*-Si:H films. The bonding of H and O atoms in the ternary alloys *a*-Ge:(H,O) is also different from what has been reported for the corresponding Si ternary alloys, both in the nature of the local atomic arrangements of the O and H atoms, and in the relationship between these bonding environments and the source of the oxygen atoms (O_2 or H_2O). These differences in bonding in *a*-Ge:H and *a*-Ge:(H,O) films with respect to the corresponding *a*-Si alloy films reflect differences in both the plasma-phase precursor chemistry and temperature-dependent reactions at the growth surface.

I. INTRODUCTION

There have been numerous studies of the bonding of H in *a*-Si:H alloys by vibrational spectroscopy, principally ir absorption,[1,2] with summaries of this work appearing in two recent review articles.[3,4] ir studies of the local bonding of alloy atoms in (*a*-Si)-based materials have also been extended to ternary systems including *a*-Si:(H,O),[5,6] *a*-Si:(H,N),[6,7] *a*-Si:(H,C),[8] and *a*-Si:(H,Ge).[9–11] Binary alloys of Ge and H and ternary alloys of Ge, H, and O have to date received much less attention,[12–15] but are of current interest in light of attempts to produce *a*-Si:(Ge,H) alloys for photovoltaic applications. Most of the studies of *a*-Ge:H alloys have been made on films produced by the reactive sputtering of Ge in a hydrogen ambient.[12–15] The films produced in this way show ir-absorption bands that have been assigned to both monohydride and polyhydride groups. However, there have been no systematic and detailed studies of H-atom bonding in films of *a*-Ge:H produced by the plasma decomposition of germane, or of ternary alloy films containing O as well as H produced by any method. This paper presents a study of *a*-Ge:H and *a*-Ge:(H,O) films prepared by the plasma decomposition of germane, and germane and O_2 and/or H_2O mixtures, respectively, at relatively high power levels (the so-called glow-discharge or GD method). We have studied the atomic bonding of the alloy atoms H and O by ir absorption. We compare the ir spectra and their interpretation, with what has been reported for: (1) *a*-Ge:H produced by reactive sputtering, and (2) *a*-Si:H and *a*-Si:(H,O) produced by the GD method. We find substantive differences between the incorporation of H in *a*-Ge:H films produced by sputtering and the GD process, as well as differences in the incorporation of H and O in ternary alloys of *a*-Ge:(H,O) as compared to the incorporation of the same alloy atoms in *a*-Si:(H,O) alloys. The bonding geometries that we have found for H and O in the *a*-Ge alloy films are related to aspects of plasma-phase and surface-reaction chemistry that are qualitatively different from what occurs in the deposition of *a*-Si films from silane-based plasmas. We believe that an important contribution to these differences in solid-state bonding derives from differences in the nature of the precursor species generated in germane- versus silane-based plasmas.

II. FILM PREPARATION AND CHARACTERIZATION

Binary alloys of *a*-Ge:H were prepared by the glow-discharge decomposition of pure germane, GeH_4, in a conventional system which is described elsewhere.[5] The rf input power was maintained at 10 W, and the pressure at 0.5 Torr. The electrode spacing in this system is about 1 cm and the electrode diameters are approximately 1 in., corresponding to a power density of 5 W/cm^2, or 5 W/cm^3. Ternary alloys of *a*-Ge:(H,O) were prepared via the glow-discharge process at the same input power and pressure, and with two different sources of oxygen atoms: (1) by mixing O_2 and GeH_4 in the plasma chamber (but from two separate sources), and (2) by growing films from GeH_4 in a chamber containing small amounts of water vapor. Alloy films were deposited with substrate temperatures T_s held between 50 and 450 °C. Films were grown on high-resistivity ($>10\ \Omega\,\mathrm{cm}$) crystalline Si substrates, primarily for the ir studies, but also equally useful for electron microprobe measurements, and on fused silica substrates for a measurement of film thickness. The film thickness, typically 1 μm, was determined by an interferometric technique. The oxygen composition in the films was obtained by electron microprobe analysis, and the H concentration by the integrated ir absorption in the bond-bending absorption band at 560 cm^{-1}.[13,14] Infrared spectra were obtained using a Perkin Elmer model no. 580B (PE 580B) double-beam ratio recording spectrophotometer.[5,7] Spectral resolution was approximately 3 cm^{-1}, and the transmission data are accurate to $+0.5\%$. The PE 580B was used in conjunction with a PE model no. 3600 Data Station with software for analyzing spectral data for obtaining the optical constants and the integrated ir absorption.

III. EXPERIMENTAL DATA AND DATA REDUCTION

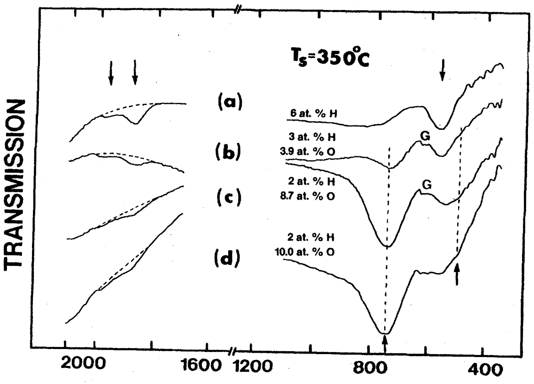

FIG. 2. ir-absorption spectra for a-Ge:(H,O) alloys grown by adding O_2 to the germane in the plasma discharge, and with $T_s = 350\,°C$. The downward arrows indicate Ge—H vibrations and the upward arrows Ge—O vibrations. The concentrations of bonded H and O are indicated.

Figure 1 contains ir-absorption spectra for four films of a-Ge:H produced via the glow-discharge decomposition of GeH_4 for substrate temperatures of 100, 250, 300, and 400 °C. The features at approximately 1880 and 560 cm^{-1} have previously been assigned to the bond-stretching and bond-bending vibrations, respectively, of monohydride bonding groups,[12–14] while the band at 2000 cm^{-1} and the doublet at 765 and 825 cm^{-1} have been ascribed to dihydride groups.[2,13–16] The dihydride groups also contribute to the bending vibration at 560 cm^{-1}.[13,14] It is clear that monohydride bonding dominates at high T_s, while dihydride bonding becomes increasingly important as the substrate temperature is decreased. The amount of bonded hydrogen obtained from the integrated absorption in the 560 cm^{-1} band is also shown in the diagram. Figure 2 gives the ir absorption for four films grown at 350 °C, with different amounts of oxygen added to the plasma. Trace (a) is for a film grown without oxygen and traces (b) through (d) are for oxygen/germane gas-phase mixtures (O_2 /GeH_4) ranging from 5% to 50%. The concentrations of bonded H and O atoms are indicated on the diagram. There are two points to note with respect to the ir spectra of these ternary alloys: (1) the oxygen features (marked with dashed lines) at 750 and 500 cm^{-1} grow with increasing oxygen gas added to the plasma mixture, as expected; but (2) this is accompanied by a decrease in the strength of the ir bands associated with H incorporation, not expected on the basis of results reported for a-Si:(H,O) alloys where the amount of bonded H increases with increasing O incorporation.[5] Qualitatively similar effects, relative to the respective O and H concentrations, occur in a-Ge:(H,O) films prepared at lower substrate temperatures. Figure 3 illustrates the effects of adding O_2 to amorphous films grown at $T_s = 100\,°C$; trace (a) is for no oxygen added, and traces (b) and (c) are for increasing amounts of O. As in the films grown at 350 °C, the bonding of O gives rise to characteristic ir-absorption bands: one near 750 cm^{-1} (in part obscured by the Ge—H doublet at 765 and 825 cm^{-1}), a second band at approximately 500 cm^{-1} and a third at about 670 cm^{-1}. The third band at 670 cm^{-1} is present only in low T_s alloys, those produced with substrate temperatures maintained

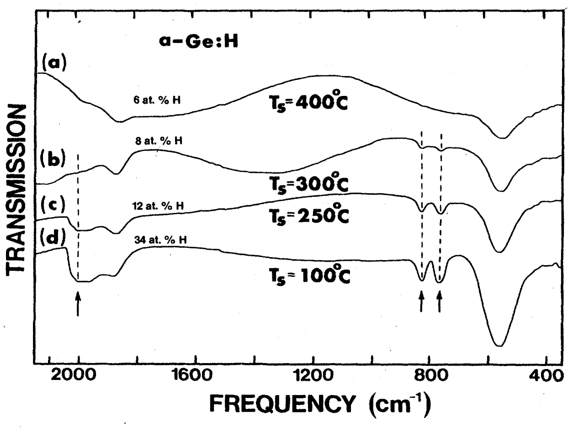

FIG. 1. ir-absorption spectra for a-Ge:H alloys for substrate temperatures of 100, 250, 300, and 400 °C. Bonded H-atom concentrations are indicated. The dashed lines and arrows denote the absorption bands associated with polygermane bonding groups.

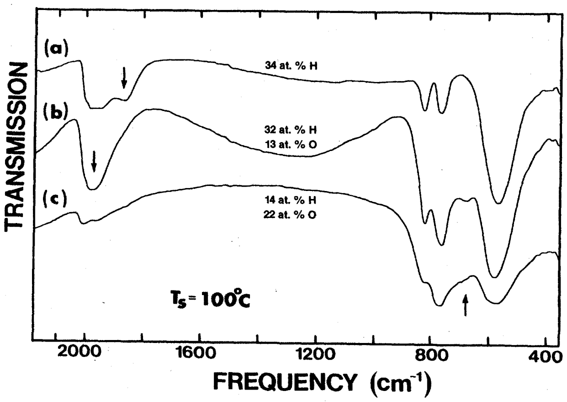

FIG. 3. ir-absorption spectra for a-Ge:(H,O) films grown by adding O_2 to the germane with $T_s = 100\,°C$. The concentrations of bonded H and O are given for each trace. The arrow in trace (a) denotes the GeH bond-stretching absorption, the arrow in trace (b) the polygermane bond-stretching absorption, and the arrow in trace (c) the absorption of 670 cm^{-1} which is associated with O and H atoms bonded at the same Ge site.

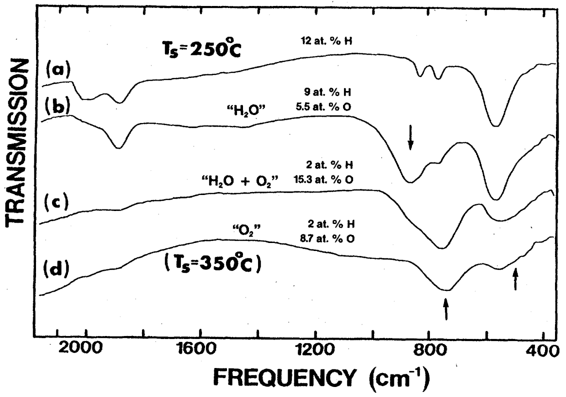

FIG. 4. ir-absorption spectra for *a*-Ge:(H,O) alloys grown by adding either or both O_2 and H_2O to the germane plasma. The upward arrows indicate the Ge—O vibrations derived from adding O_2 to the plasma and the downward arrow indicates the Ge—O vibration associated with film growth in the presence of H_2O.

below about 225 °C (the temperature for the onset of strong polyhydride bonding; see Fig. 1). As in the spectra for $T_s = 350\,^{\circ}C$ films of Fig. 2, the H-related features decrease in strength as more O is incorporated into the film.

Figure 4 illustrates differences in the Ge—O vibrations in *a*-Ge:(H,O) alloys that derive from different sources of O atoms; either O_2 mixed with the GeH_4, or residual water vapor in the deposition chamber. Trace (a) is a reference spectrum for $T_s = 250\,^{\circ}C$, and shows both monohydride and dihydride Ge—H absorption bands. Trace (b) illustrates changes in the absorption that derive from residual water vapor in the deposition chamber. The main effects of this background pressure of H_2O on the ir spectrum are as follows: (1) the appearance of a new Ge—O feature at 860 cm^{-1}; and (2) a reduction in the H incorporation, primarily in the dihydride bands. Trace (c) indicates the changes derived from mixing O_2 with the GeH_4 and not baking out the chamber (H_2O is then a second source of bonded oxygen). For this case both types of Ge—O bands are evident: (1) the bands at 750 and 500 cm^{-1} discussed with reference to Fig. 2, and (2) the band at 860 cm^{-1} discussed with respect to trace (b) of this diagram. Trace (d) illustrates the effect of adding O_2 to the gas mixture, but baking out the chamber to remove residual H_2O. This produces the bands 750 and 500 cm^{-1}, similar to spectral features shown in Fig. 2. Figure 5 gives the ir bands for a more extensive spectral range for two types of *a*-Ge:(H,O) films, grown with either O_2 or H_2O. Trace (a) displays data for a film with $T_s = 300\,^{\circ}C$ grown in a chamber with residual H_2O and trace (b) for a film grown at $T_s = 400\,^{\circ}C$, but with O_2 as the source of the oxygen incorporation. The film in trace (a) shows two oxygen-related features at 860 and 560 cm^{-1}, with the possibility of a weak third feature at about 300 cm^{-1}. The film in trace (b) shows three O-related features as bands centered at 750, 500, and 300 cm^{-1}.

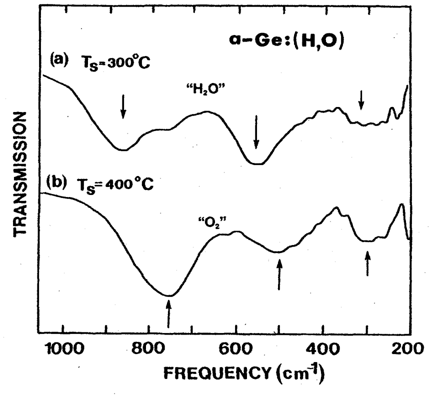

FIG. 5. ir-absorption spectra for *a*-Ge:(H,O) alloy films grown with either H_2O [trace (a)] or O_2 [trace (b)] added to the germane in the plasma discharge. The arrows indicate the Ge—O vibrations.

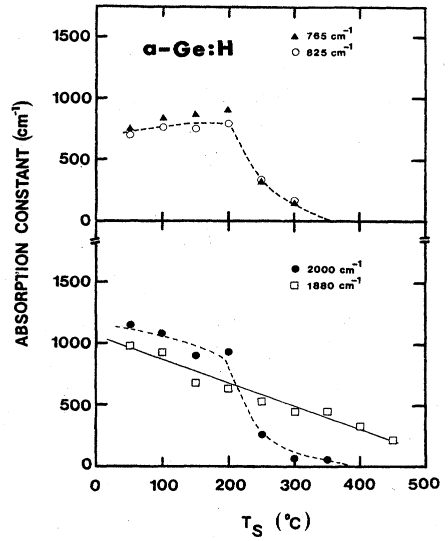

FIG. 6. ir-absorption constants for the 1880 cm^{-1} bond-stretching vibration of GeH groups, the 2000 cm^{-1} bond-stretching vibration of polygermane groups, and the 765 and 825 cm^{-1} wagging and/or scissors vibrations of polygermane groups as a function of T_s. The lines connecting the points indicate the trends with T_s.

Figure 6 gives the temperature dependence of the monohydride and dihydride bands in the *a*-Ge:H alloy films. The data are derived in part from the spectra shown in Fig. 1, and also from other depositions made at intermediate substrate temperatures. The lower trace compares the temperature variation of the peak values of the absorption constants at 1880 and 2000 cm^{-1}, the stretching modes, respectively, of monohydride and dihydride groups.[12–16] The upper trace tracks the temperature dependence of the dihydride doublet feature at 765 and 825 cm^{-1}. The aspects of these curves we wish to emphasize are (1) the relatively sharp T_s threshold for dihydride bonding, and (2) the continued increase in monohydride bonding for T_s decreasing below the threshold for dihydride incorporation. These variations of absorption strength as a function of T_s in Fig. 6 are to be compared with those for the corresponding vibrations in *a*-Si:H alloy films as shown in Fig. 4 of Ref. 2. The

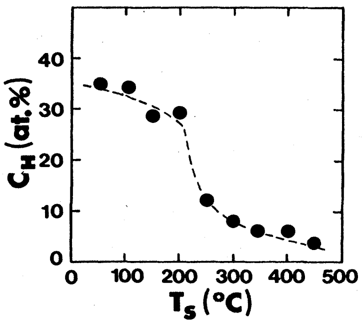

FIG. 7. Bonded H-atom concentration as a function of T_s for *a*-Ge:H alloy films.

trends shown in Fig. 6 for the deposition of *a*-Ge:H alloys at high-power density are qualitatively different from the Si data obtained at lower-power levels and for a silane plasma diluted by argon. For the Si case, there is a clear "competition" between monohydride and dihydride bonding, and the absence of a distinct temperature threshold for dihydride incorporation.[2] Figure 7 is a plot of the total bonded H-atom concentration as a function of T_s. The sharp increase from a level of about 10 to 12 at. % to approximately 25 at. % at a T_s near 225 °C is due to the increased incorporation of H atoms in dihydride bonding arrangements. A similar plot of total bonded H-atom concentration versus T_s for *a*-Si:H alloys, deposited from diluted silane + argon mixtures, and at lower power levels, yields a more gradual and continuous increase of bonded H with decreasing T_s. These differences in GD deposited *a*-Ge:H and *a*-Si:H films will be discussed in terms of a model that is based on plasma phase and surface reactions. This model specifically identifies differences in the precursor plasma-phase chemistry between the low power dilute silane/argon plasmas of Ref. 2, and the high-power germane plasmas used in this work, and the role this chemistry plays in determining the differences in the local bonding of H in the deposited *a*-Ge:H and *a*-Si:H films. The model is readily extended to account for the differences between the bonding of H and O in ternary *a*-Ge:(H,O) alloys and their *a*-Si counterparts.

IV. LOCAL BONDING ARRANGEMENTS OF H AND O ATOMS

A. *a*-Ge:H alloys

Figure 8 indicates the possible local bonding arrangements for H in *a*-Ge:H alloys. We have shown a relatively complete set of bonding configurations in part A of the diagram including: (1) the isolated monohydride or GeH group, (2) the isolated dihydride or H—Ge—H group, (3) the isolated trihydride or GeH_3 group, and finally (4) the polygermane or $(GeH_2)_n$ configuration. The ir spectra shown in Fig. 1 can be explained using only two of these four possible groups with the Ge—H bonding giving rise to the bond-stretching vibration at 1880 cm^{-1} and the bond-bending vibration at 560 cm^{-1}, and the polygermane configuration giving rise to the bond-stretching vibration at 2000 cm^{-1}, the scissors vibration at 825 cm^{-1}, the wagging vibration at 765 cm^{-1}, and the bond-rocking vibration at 560 cm^{-1}.[2,16] The assignments given above parallel those proposed for *a*-Si:H alloys.[1–4] Note that in glow-discharge-deposited *a*-Si:H, one finds spectroscopic evidence for isolated as well as polymerized SiH_2 groups, whereas in *a*-Ge:H alloys grown via the high-power GD process, there is no evidence for isolated GeH_2 groups. There is evidence, however, for the isolated GeH_2 bonding arrangement in films produced via the reactive sputtering of Ge in a hydrogen ambient.[4,13–16]

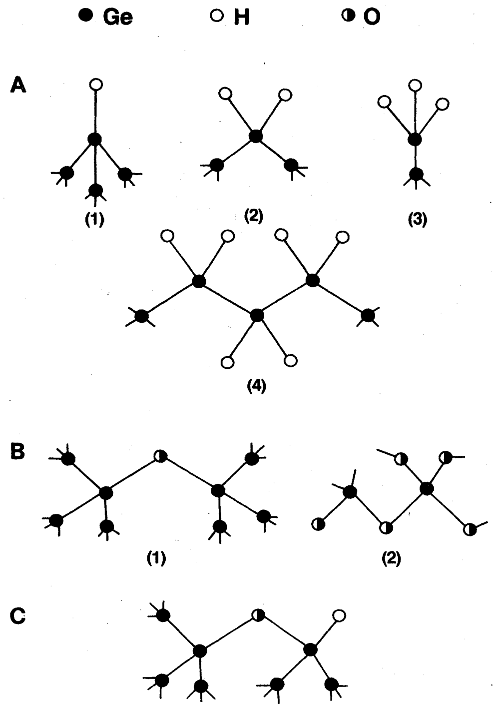

FIG. 8. Schematic representation of local atomic bonding: A, Ge—H groups, (1) monohydride, (2) dihydride, (3) trihydride, and (4) polyhydride; B, Ge—O groups, (1) isolated Ge—O—Ge group, and (2) GeO_2 bonding; and C, attachment of H and O to the same Ge site.

B. *a*-Ge:(H,O) alloys

Figure 8 also illustrates local bonding arrangements for O in *a*-Ge(H,O) alloys. There are three different arrangements that have been identified in this study. Part B of Fig. 8 indicates two of these environments. We identify the features at 750, 500, and 300 cm^{-1} that are found in films grown in the germane + oxygen mixture, with isolated Ge—O—Ge groups as shown in Fig. 8, B (1). The three absorptions at 750, 500, and 300 cm^{-1} correspond, respectively, to bond-stretching, bond-bending, and bond-rocking vibrations, There is no evidence in high-temperature alloys, $T_s > 250$ °C for any near-neighbor H-atom attachment in sequences of the general form Ge—O—Ge—H, paralleling the Si—O—Si—H sequences reported in *a*-Si:(H,O) alloys.[5,6] For alloys grown with $T_s < 225$ °C, there is evidence, however, for near-neighbor hydrogen attachment, as shown in C of Fig. 8, with the vibration at 670 cm^{-1} playing the same role as the 780-cm^{-1} vibration in a-Si:(H,O) alloys.[5,6] Part B (2) of Fig. 8 gives the local bonding arrangements responsible for the three vibrations at 860, 560, and 300 cm^{-1} found in films grown in the presence of water vapor. These vibrations correspond, respectively, to the bond-stretching, bond-bending, and bond-rocking vibrations of local atomic arrangements similar to those occurring in a-GeO$_2$.[17] A comparison between B (1) and B (2) of Fig. 8 indicates that the major difference in the two bonding groups derives from isolated Ge—O—Ge configurations in the first case, and "near-neighbor" Ge—O—Ge configurations in the second. Finally, it should be noted that there is no spectroscopic evidence for the incorporation of OH groups for either type of bonding. This last observation relative to OH groups parallels what has been found in a-Si:(H,O) alloys.[5,6]

V. MODEL FOR THE INCORPORATION OF H AND O IN *a*-Ge ALLOYS

A. *a*-Ge:H alloys

There have been many studies of the species in silane plasmas, and numerous attempts have been made to relate the incorporation of H in the deposited a-Si:H films to specific plasma-phase precursors.[18–23] Clearly there is evidence in these studies for surface as well as plasma-phase reactions being important in determining the details of the local-bonding arrangements of H in the deposited-alloy films. For example, it is reasonably well established that SiH$_3$ molecules play a key role in H incorporation, and that the number of H atoms retained per Si atom, and hence the occurrence of SiH, SiH$_2$, and possibly SiH$_3$ groups, is determined by the H atom rejection which is primarily a function of T_s.[18–21] It has also been demonstrated, that under different deposition conditions, mostly at high power, and/or using disilane, that plasma-phase polymerization becomes increasingly important, and in turn accounts for the incorporation of bonded H in polysilane groups.[23]

The incorporation of H in a-Ge:H films, for the high-power-density regime we have explored, is qualitatively similar to the incorporation of H in a-Si:H alloys at low power, but with several important differences that we attribute to details of the plasma-phase chemistry. Consider the distinct threshold for incorporation of polyhydride groups in the deposited films. We attribute the sharp T_s dependence to a dissociation of plasma-phase-generated higher germane groups. The relatively high power in the discharge for a pure germane plasma favors reactions in which monogermane groups become attached to one another and generate higher germanes, primarily Ge$_2$H$_6$ and Ge$_3$H$_8$, or fragments thereof. These groups are relatively stable in the gas phase, but will dissociate upon condensation on a high-temperature substrate. Digermane molecules are known to dissociate rapidly above about 225 °C,[24] and for films condensed near or below this temperature, they are, in our model, the plasma-phase species that undergo a surface-driven polymerization that leads to the incorporation of polyhydride groups in the condensed solid-state films. For films condensed at higher T_s, the digermane groups become dissociated at the surface, and the fraction of bonded H in polyhydride groups is sharply diminished. Higher germanes, formed in plasma are known to have lower dissociation temperatures,[25] and can only directly contribute to the solid-state bonding in films condensed below their dissociation temperatures. We then trace the incorporation of most of the polyhydride in the films to the plasma-phase generation of digermane.

Figure 6 demonstrates that the amount of bonded H in GeH groups increases approximately linearly with decreasing T_s, but shows no change in slope near the dissociation temperature of digermane. We take this to infer that the GeH groups enter the film through a different precursor molecular group. We assume that this group is a hydrogen-deficient germane, for example, GeH$_3$, GeH$_2$, or GeH. In our model the branching ratio between the generation of these groups and higher germanes (digermane and above) is determined by the conditions in the germane discharge, and the incorporation of H in the film in GeH and (GeH$_2$)$_n$ groups is then determined by this branching ratio as well as surface reactions that (1) in the case of GeH incorporation, determine the fraction of the H that is retained in the film as it grows at a given T_s, and (2) in the case of polyhydride incorporation, by reactions at $T_s > 225\,^\circ\mathrm{C}$, which dissociate the digermane and do not lead to bonded H in the films, or at lower T_s, condense the digermane in longer polyhydride groups that become incorporated in the growing film. We are currently studying the properties of a-Ge:H films grown by the GD method at lower power, and for germane diluted with hydrogen. The initial results of these studies support the model discussed above, and will be reported elsewhere.[26]

The model discussed above can be represented by the following schematic equations. We assume a branching ratio, designated by the coefficient a and b, such that

$$a\,\mathrm{GeH_4} \rightarrow \text{lower germanes } (\mathrm{GeH, GeH_2, GeH_3}) + \mathrm{H_2}\ ,$$

and

$$b\,\mathrm{GeH_4} \rightarrow \text{higher germanes (mostly } \mathrm{Ge_2H_6} \text{ and } \mathrm{Ge_3H_8})\ ,$$

where $a+b=1$. The fraction of GeH groups in the films is then determined by a and T_s, while the fraction of polygermane in the films is determined by b and T_s. For the incorporation of H in GeH groups, the amount of H retained is a nearly linear function of decreasing T_s, and furthermore, the probability of retaining more than one H per Ge appears to be small. For the incorporation of the polygermane groups, the surface or substrate temperature plays a key role. At high $T_s > 225\,^\circ\mathrm{C}$, it contributes to a dissociation of digermane and any higher germanes, and hence greatly reduces the incorporation of polymer groups. For lower T_s, the digermane is not dissociated, and surface-induced polymerization becomes the process by which polygermane groups are incorporated into the growing film.

B. a-Ge:(H,O) alloys

The incorporation of O into *a*-Ge:(H,O) alloys can be understood by an extension of our model in which Ge—O precursors are formed at the expense of Ge—H precursors. We have observed that the bonding of O in *a*-Ge alloys is different for the source of O atoms being O_2 or H_2O. This is qualitatively different from the incorporation of O in *a*-Si:(H,O) alloys, wherein both sources of oxygen yield the same local bonding of O atoms in the films.[5,6] *a*-Ge:(H,O) alloys also differ in other respects when compared to the *a*-Si:(H,O) alloys. We attribute these differences to plasma-phase interactions. Before discussing a specific model, we review some of the properties of the *a*-Si:(H,O) alloys, in particular the way H and O are bonded, and the insights that this provides for understanding the relationship of bonding in the films to the plasma-phase chemistry. The following aspects of O-atom bonding are to be noted: (1) O and H always occur as second neighbors in local-bonding arrangements of the type indicated in Fig. 8, part C.[5,6] (2) The incorporation of O does not compete with, and/or diminish the incorporation of H, in fact the incorporation of O may even increase the amount of bonded H.[5] (3) There is no evidence for OH bonding groups.[5] These characteristics of O incorporation in *a*-Si:(H,O) alloys can be understood in terms of a model in which the precursor molecule important for O incorporation in *a*-Si:(H,O) alloys is disiloxane, or a fragment thereof. This molecule can be generated via the plasma-phase interaction of either O_2 or H_2O with silane through a reaction of the type given below:[27]

$$SiH_4 + O_2 \text{ (or } H_2O) \rightarrow H_3Si{-}O{-}SiH_3 \; .$$

O is then incorporated in the film by the attachment of these molecules at the surface. The attachment is accompanied by rejection of most of the H, except for the spectroscopic observation that each O atom has at least one, and generally not more than two, second-neighbor H atoms in a geometry of the type shown in Fig. 8, part C. In addition to disiloxane, other Si-H molecules are also generated, as in plasmas without added O_2 or H_2O, and these serve as the plasma-phase precursors for the incorporation of H in the other Si—H bonding groups such as SiH, SiH_2, $(SiH_2)_n$, etc. The absence of OH groups in *a*-Si:(H,O) alloys derives from the fact that Si alcohols are not stable[27] and convert to disiloxane via reactions of the types shown below:

$$H_3Si{-}OH + SiH_4 \rightarrow H_3Si{-}O{-}SiH_3 \; ,$$

or

$$2(H_3Si{-}OH) \rightarrow H_3Si{-}O{-}SiH_3 + H_2O \; .$$

For the *a*-Ge:(H,O) alloys discussed above, we find qualitatively different results which are summarized below: (1) The incorporation of O in *a*-Ge:(H,O) alloys is different for different sources of oxygen atoms (O_2 or H_2O). (2) In either case, the bonding of O is "competitive" with the incorporation of H. (3) There is no evidence for OH groups in the films. (4) There is evidence for Ge—O—Ge—H sequences, but only for low-T_s films ($<225\,^\circ C$) grown in the presence of O_2. These observations lead to the following generalizations: (1) The plasma-phase reactions between germane and O_2 and H_2O lead to different molecular precursor species, which in turn may undergo different types of surface reactions. (2) In either case the precursor molecules that are formed serve to deplete the plasma of the precursors that are responsible for H-atom incorporation. (3) Reactions that may give rise to OH groups are not favored.

The reactions discussed above for the incorporation of H in *a*-Ge:H alloys and the model reactions for O uptake in *a*-Si:(H,O) films lead to the following model for the growth of *a*-Ge:(H,O) films. We assume that both O_2 and H_2O react with Ge-H species in the plasma phase and thereby effectively reduce the fraction of the germane that is converted to both lower and higher germanes, i.e., GeH, GeH_2, GeH_3, and Ge_2H_6, Ge_3H_8, etc., respectively. These precursors are replaced by molecules or radicals with Ge—O bonds, which in turn condense at the growth interface and lead to Ge—O bonding groups in the film. The study that we have made of the local bonding of O in the films as a function of the O-bearing gas added to the germane implies that the precursor species are different for O_2 and H_2O.

We now present a specific model which accounts for the competition between H and O incorporation in the *a*-Ge:(H,O) films. The model is based on the strong reaction that occurs between digermane and oxygen.[25] This reaction proceeds rapidly for temperatures greater than $100\,^\circ C$, even in the absence of a plasma discharge,[25] and we make the assumption that the reaction proceeds even more readily in a glow discharge of digermane and oxygen. The model is described by the two gas-phase reactions given below:

$$GeH_4 \rightarrow a'GeH_x + b'Ge_2H_y$$

and

$$Ge_2H_y + O_2 \rightarrow Ge{-}O{-}Ge \; ,$$

where a' and b' are constants that characterize the reaction branching ratio under a particular set of glow-discharge conditions, x and y characterize generalized monomer and dimer species respectively, and Ge—O—Ge represents a molecule (or radical) species that is the precursor for the Ge—O—Ge groups that eventually get incorporated into the deposited thin film alloy. The second of the two reactions depletes the supply of Ge_2H_y formed by the first reaction, and in this way effectively reduces the concentrations of both the monomer and dimer species, GeH_x and Ge_2H_y, respectively. We have already noted that bonded monohydride and polymerized dihydride groups in the films are derived, respectively, from these monomer and dimer groups. Therefore, the strong reaction between digermane and O_2 drives the pair of reactions in such a way that the monomer and dimer groups produced by the plasma decomposition of germane are consumed at the expense of forming Ge—O—Ge bonding groups. We extend these equations to include a reaction between digermane and water which also proceeds rapidly in the plasma phase. The results that we have obtained for films grown in germane $+O_2$ and/or germane $+H_2O$ mixtures have demonstrated that there are two types of

Ge—O—Ge environments in the films. In the context of our model, we assume that each of these environments is derived from a different plasma phase precursor species, one of which may be similar to disiloxane, e.g., the digermoxane molecule or a fragment thereof. The occurrence of the two different Ge—O bonding groups implies that in the germane plasma environment, the digermane molecule reacts differently with O_2 and H_2O. This behavior is different from silane-based plasmas wherein the inclusion of either O_2 or H_2O in the silane plasma leads to the same local bonding in the solid. Within the framework of our model, this Si—O—Si—H bonding group then derives from the same plasma-phase precursor species. We are currently embarking on a study of plasma-phase interactions using mass spectrometry as a probe to identify the plasma-phase reaction products. This technique has worked for pure-silane plasmas, and is being extended to germane-based plasmas as well.

C. Glow-discharge deposition of *a*-Ge and *a*-Si alloys

In the context of the models discussed above, the differences between the local bonding of H and O in *a*-Ge alloys and *a*-Si alloys derive from differences in plasma-phase chemistry and T_s-dependent surface reactions involving these plasma-phase precursor species. The most important factors are generally different reaction paths, which lead to qualitatively different precursor species. One important result of this study is a demonstration of correlations between specific solid-state bonding arrangements involving the alloy atoms, and specific plasma-phase precursors.[16] These types of correlations are dominant for local bonding groups in which there is a close association of alloy atoms, e.g., more than one alloy atom per Ge (or Si) atom, as in polymerized dihydride groups, or in sequences of the form Ge—O—Ge—O—Ge or Ge—O—Ge—H, etc. The correlations between solid-state bonding and specific precursor species are not as important for monohydride bonding, as has already been noted in Ref. 26. For these groups, H-atom rejection via T_s-dependent surface reactions appears to be the dominant mechanism limiting the amount of monohydride bonding in a given film, and the source of the monohydride groups cannot generally be linked to one specific precursor species. Nevertheless, it should be noted that at least for *a*-Ge:H alloys grown from germane plasmas at high-power levels, and for films deposited with T_s less than 200 °C, the total amount of H available for incorporation in monohydride bonding is limited by plasma-power-dependent branching ratios which determine the relative amounts of monomer and dimer species that are generated in the discharge. In this model, the monohydride groups are derived from any one of several monomer groups such as GeH, GeH_2, or GeH_3. In films deposited above 250 °C, the thermal dissociation of the plasma-phase-generated polymer (or digermane) at the film surface does not appear to contribute significantly to the concentration of monohydride groups in the deposited films. For the case of O incorporation, the plasma-phase precursors with Ge—O—Ge linkages deplete the plasma of the precursors that provide H-atom incorporation in both monohydride and dihydride groups. In the silane plasmas, this is not the case; H-atom incorporation readily occurs, and can even increase in the presence of O through the route described above, i.e., through the incorporation of Si—O—Si—H sequences that derive from disiloxane generated in the plasma and incorporated into the film via reactions at the growth surface.

VI. SUMMARY

We have measured the concentration, and studied the bonding configurations of the elements H and O in *a*-Ge:H and *a*-Ge:(H,O) films prepared by the glow-discharge decomposition of germane (with and without O_2 and/or H_2O at varied partial pressures) over a substrate temperature range of 50 to 450 °C. In contrast to similar studies of the *a*-Si:H and *a*-Si:(H,O) systems, we observe (1) an absence of isolated dihydride groups, (2) a temperature threshold of approximately 225 °C, above which the polyhydride density is sharply reduced, and (3) a distinct competition between Ge—H and Ge—O bonding (i.e., a reduction of the H concentration in film as the O concentration in that film is increased). These differences between the Si- and Ge-alloy systems are attributed to differences in both plasma-phase and surface chemistry.[28] The plasma-phase reactions are thought to include a polymerization of germane to form higher germanes. A surface reaction of importance is the thermal decomposition of higher germanes which occurs for surface temperatures above about 225 °C. In the case of germane plasmas containing either O_2 or H_2O, reactions with plasma-generated higher germanes occur. In the context of our model, they provide the reaction path for the generation of precursor species through which Ge—H bonds are replaced in the films by Ge—O bonds. In all cases, further studies of plasma-phase interactions, as well as film growth under different deposition conditions are needed in order to identify the specific plasma-phase precursors, and the microscopic mechanisms that are responsible for incorporation of particular types of H- and O-alloy atom bonding groups in the deposited films.

ACKNOWLEDGMENTS

The authors wish to acknowledge: stimulating discussions with Dr. R. Tsu, Dr. S. Hudgens, and S. R. Ovshinsky, the constant encouragement and support of S. R. Ovshinsky, technical assistance of L. Christian, L. Taylor, and L. Contardi, and partial support for this work from the Standard Oil Company (Ohio).

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