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STRUCTURAL PROPERTIES OF GLOW DISCHARGE a-Sil-x^{Ge}x:H ALLOYS AS REVEALED BY INFRARED ABSORPTION AND HYDROGEN EVOLUTION TECHNIQUES^{*} D. K. Paul[†], B. von Roedern, S. Oguz, J. Blake and W. Paul Gordon McKay Laboratory

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We report results of infrared vibrational absorption and H evolution measurements made on thin films of hydrogenated Si $_{1-x}$ Ge prepared by dc-glow discharge decomposition of SiH₄ and GeH₄. We find a significant amount of weaklybonded H in pure Ge and Ge-rich alloys, and a preferential attachment of H to Si atoms. A heterogeneous structural model is proposed to explain the results.

I. Introduction

There are at least three reasons to study amorphous hydrogenated silicongermanium alloys (a-Si_Ge:H). (1) Since Si and Ge are known to form an amorphous, random, tetrahedrally-coordinated alloy [1], this system is the simplest, prototypical, hydrogenated binary. Although several hydrogenated binaries have been investigated [2,3], it does not seem always to have been recognized that extrapolation of properties from the hydrogenated elements will not be straightforward if the two constituents have different bonding properties with H. (2) Between the hydrogenated elements Si and Ge there are many similarities: with increasing H-content, decreased electron spin resonance, increased optical gap, decreased conductivity at all T, activated transport, improved photoconductivity are observed. Nevertheless, there are also gross dissimilarities: for example, a-Ge:H shows no field effect, indicating a much higher pseudogap state density, it has never been reported to show photoluminescence, and its photoconductive response is orders of magnitude poorer than that of the best a-Si:H. These fundamental differences are not understood, but they need to be if a comprehensive understanding of either element is to be attained. Study of the alloy as a function of x is one means to this end. (3) Some applications, for example, solar cell technology, would find useful the possible tuning of the band gap by altered composition, independent of H, but without concomitant deterioration in properties.

II. Preparation and Characterization

We prepared many co-deposited samples of different x, thickness from 0.2 to 12 μ m, on substrates of Corning 7059 glass, c-Si and quartz, held at 100 or 250°C, by dc-glow discharge decomposition of different-ratio mixtures of pure GeH₄ and SiH₄ [4]. The total pressure of (GeH₄ + SiH₄) was kept constant from run to run. The rate of deposition, for the same applied power, then increased monotonically with x from 0.1 μ m/min. for x = 0 to 0.5 μ m/min. for x = 1. The amorphicity of the films was verified by X-ray diffraction. The composition, x, was checked by electron microprobe to be uniform across the film within the instrument sensitivity of 1%. Secondary ion mass spectrometric examination (SIMS) showed uniform bulk densities of oxygen less than 0.5% and of carbon less than 0.1%. Sometimes, within 500 Å of the film-c-Si substrate interface, an increase of the 0 and C content by an order of magnitude was observed. However, it is unlikely that any properties were substantially

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altered since Si-0 infrared vibrational absorption was not observed even in the 12 μ m-thick films. SIMS also confirmed the uniform depth profiles of H, Si and Ge. TEM and SEM micrographs showed smooth, homogeneous regions with no evidence of columnar growth in the magnification range available, but this in itself does not guarantee the absence of heterogeneity. Although an attempt is being made to interpret many properties (structural, optical absorption, UV reflectivity, photoconductivity, photoluminescence, electrical [4], we shall concentrate here on what evidence there is contransport) cerning the H content and distribution since these are important questions to be settled before the dependent properties can be sensibly examined. In brief, however, the electronic and optical properties change monotonically, although non-linearly, as the composition of the plasma is changed. Thus, when no corrections for possible alterations with x of the H-content are considered, the optical absorption edge displaces to lower energy, at first slowly, then more rapidly, as x is increased; the conductivity activation energy follows the same pattern, remaining essentially unchanged at 0.85 eV for x < 0.5 and then decreasing to 0.5 eV for x approaching 1; the photoconductivity, on the other hand, decreases rapidly as x increases from 0, and reaches roughly the value for pure a-Ge:H for x = 0.5; and the magnitude of the photoluminescence decreases by more than two orders with increasing x, becoming unmeasurable in our apparatus for $x \approx 0.8$. We regard these results as reasonable, but preliminary, capable of quantitative interpretation only after the chemical and structural details are settled.

III Selected Properties

We concentrate next on the infrared vibrational absorption spectra, the evolution of H upon heating, and the remeasurement of infrared spectra at intermediate stages of annealing.

Figure 1 shows a selection of spectra of the evolution of H from a-Ge:H, a-Si:H and three alloys. From such spectra and the total pressure of H evolved we conclude (1) the concentration of H in the alloys is higher than in either a-Si:H or a-Ge:H (2) whereas the H in a-Si:H evolves at T > 400°C, a significant fraction of that in a-Ge:H comes out near 150°C (3) the evolution spectra of the alloys are intermediate and favor the spectra of the dominant component.

The infrared absorption spectra of the films were measured in the asdeposited condition, and after successive anneals at 150, 190 and 250°C. Representative behavior is illustrated in Fig. 2 for a-Ge:H and a-Ge_{0.7}Si_{0.3}:H deposited at 100°C. The integrated area under the wag modes near 600 cm⁻¹ was used to estimate the content of bonded H, assuming equal matrix elements for absorption by Si-H and Ge-H bonds, given by the results of the Stuttgart group [5]. The absorption in the



Figure 1. Evolution of H from a-Si_{1-x}Ge_x:H alloys

group [5]. The absorption in the 1-X X stretch modes near 2000 cm⁻¹ was deconvoluted to give the relative absorption caused by Si-H and Ge-H bonds, assuming the matrix elements are not changed by the local environment, and correcting for the relative Ge/Si contents given by microprobe analysis. From these studies we can conclude (1)



Figure 2. Infrared absorption in a-Si_Ge :H alloys: The effects of successive anneals at 150, 190 and 250°C are shown. Spectra remain unchanged by annealing up to 190°C in SiGegd-12. Besides the appearance of the oxide band, the spectra is otherwise unchanged by annealing at 150°C in Gegd-4.

annealing a-Ge:H to about 150° C evolves a considerable amount of H, without affecting the infrared absorption spectrum. This effect is present, but less marked, in the alloys. We conjecture that it is due to very weakly bonded H in the films. (2) The concentration of bonded H estimated from the infrared modes at 600 cm⁻¹ is, in many cases, considerably less than that found from evolution. This is consistent with the existence of weakly-bonded H, especially in a-Ge:H and Ge-rich alloys. (3) Evaluation from the stretch modes of the quantity.

integrated	Si-H	absorption		Ge	content		OSC.	strength	Ge-H	(7)
integrated	Ge-H	absorption	X	Si	content	x	osc.	strength	Si-H	(1)

gives values of about 10 for all of the films, indicating that H is preferentially attached to the Si atoms. The details are given in Table 1._1 Attention is drawn to the growth of Ge-O vibrational absorption near 860 cm⁻¹ in the a-Ge:H films, an effect not observed for a-Si:H or for the alloys. This band first appears with annealing at 150°C, and is taken to reflect a difference in microstructure between the a-Ge:H and the Si-alloy films prepared in our glow discharge apparatus.

Table 1 Hydrogen content in a-Sil-x Ge: H alloys: Preferential H attachment to Si atoms as defined in (1) is included.

Sample a-Si _{l-x} Ge _x :H	Deposition Temperature T _s (^o C)	Estimated H Evolution Experiment	Preferential H Attachment		
Gegd-4 x = 1	100	10	5	-	
SiGegd-12 $x = 0.70$	100	38	23	10	
Sigd-10 x = 0	100	15	12		
Gegd-2 x = 1	250	9	3	-	
SiGegd-9 x = 0.82	250	18	9	13	
SiGegd-8 x = 0.68	250	10	9	12	
SiGegd-13 x = 0.14	250	15	9	-	
Sigd-4 x = 0	250	8	11	-	

IV. Discussion

We now put forward a tentative model for these observations, which originates in the generally-observed hetero-structure of films deposited from vapors, the particular observations of columnar structure of Knights and Lujan [6] on a-Si:H films produced by glow discharge and the confirmatory experience of our own laboratory in evaluating the transport and other properties of r.f. sputtered a-Si:H alloys. We suppose that both a-Si:H and a-Ge:H nucleate and grow in islands which eventually seek to join together. We also suppose that the H-attachment is stronger in Si so that Si-H bonds on the surfaces of islands are preferred to reconstructed Si-Si bonds as the film grows. These are harder to preserve on the surfaces of Ge islands, because reconstructed Ge-Ge long bonds often win out, and H can get trapped in the tissue. This weakly-bonded H is readily evolved at low temperatures. The Si-rich films grow in such a way that the surfaces of the islands are coated with Si-H bonds, so that there is little weaklybonded H to be evolved at low temperatures. This model explains (1) the evolution of much weakly-bonded H from a-Ge:H; (2) the smaller evolution of weakly-bonded H from alloys rich in Si; (3) the decreasing fraction of bonded H as the Ge fraction increases; (4) the preference ratio of 10:1 for Si over Ge for H in the bonded form. It also explains the poorer photoelectronic properties of the alloys and a-Ge:H itself; to the extent that this is attributable to the poorer compensation of dangling-bond defects in the islands and the tissue, it is irremediable with H, but might be with 0 or F.

Finding H preferentially attached to one element of a random binary is not new in the amorphous semiconductor literature, as it apparently occurs in $a-Si_{1-x}C_x$:H [3]. It should be noted that this may imply that defects are preferentially associated with the unfavored element. It would seem natural to look for the reason for the inferior photoelectronic performance of a-Ge:H compared with a-Si:H in a higher density of gap states in a homogeneous network of the former. The present results suggest that, at least for our conditions of glow discharge preparation of the elements and binaries, the effects of increased heterogeneity must first be weighed, for the same structural network that permits great incorporation of weakly bonded H is also likely to be full of defects yielding a high density of pseudogap states.

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