not satisfied here, this formula has only a qualitative meaning.

[15] A. I. Larkin and Yu. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. 73, 299 (1977) [Sov. Phys. JETP 46, 155 (1977)].

[16] The notation is the same as in Ref. 12 except for the omission of the superscript (L) which refers to the (L) mode. See also the article of one of the authors (A. S.) in Ref. 1.

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[18] In the opposite case $\Delta \ll T$, the driving term proportional to $\delta\dot{\Delta}$ is essential. The relaxation of the order parameter close to T_c depends entirely on this term.

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[20] For these parameters, we find that $1/\tau(\Delta) = 2.0 \times 10^9$ (for Pb), 1.7×10^8 (for Sn), and 0.9×10^6 (for Al). [The expected values of the collision rates and other data are extracted from S. Kaplan, C. C. Chi, D. N. Langenberg, J. J. Chang, S. Jafarey, and D. J. Scalapino, Phys. Rev. B 14, 4854 (1976).] Thus, we expect, in general, to have much lower frequencies in this experiment than in the experiment of Ref. 7.

Preferential Attachment of H in Amorphous Hydrogenated Binary Semiconductors and Consequent Inferior Reduction of Pseudogap State Density

W. Paul, D. K. Paul, B. von Roedern, J. Blake, and S. Oguz
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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Hydrogen evolution and infrared vibrational absorption have been interpreted to show (1) the existence of weakly bonded H in a-Ge:H and Ge-rich a-Si-Ge:H alloys, and (2) a preference ratio in excess of 5 for the attachment of H to Si over Ge in the formation of such alloys. It is suggested that this may account for the inferior photoresponse of hydrogenated binaries compared to elements, and also for the superiority of a-Si:H over a-Ge:H. Some ideas on better compensators than H are advanced.

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The presence of hydrogen during the deposition of thin films of amorphous tetrahedrally coordinated semiconductors has become an accepted means for reducing the density of defect-related states in the pseudogap.[1] It has been shown from electron-spin-resonance measurements that the dangling-bond density can be reduced by orders of magnitude. It is further expected that the density of other types of defect (such as reconstructed weak bonds) may also be reduced. Although the gross effects of H incorporation are clearly the same for all hydrogenated elements and binaries of the fourfold-coordinated system, there are quantitative differences distinguishing a-Si:H from the rest. The differences between a-Si:H and a-Ge:H, which seem to be independent of whether the material is produced by sputtering in an Ar-H plasma or by glow-discharge decomposition, are illustrated by the following typical results: The lowest reported spin density and the lowest (field effect) gap density of states are each about two orders of magnitude lower in a-Si:H than in a-Ge:H; and, while there is efficient photoluminescence in a-Si:H, none has yet been reported for a-Ge:H. It also appears that alloying some C or Ge into Si in amorphous binary alloys quickly reduces the effectiveness of hydrogenation. Yet such alloying is naturally thought of as a way of adjusting the energy gap for specific applications, such as solar cells, by analogy with crystalline material. In order to probe the reasons for the superiority of a-Si:H, we have prepared a series of hydrogenated $\mathrm{Si}_{1-x}\mathrm{Ge}_x$:H alloys by dc glow-discharge decomposition of different ratio mixtures of pure GeH_4 and SiH_4. In this communication, a carefully selected set of measurements will be interpreted, together with earlier work[2] on a-GaAs:H, and a-Si:H (Ref. 3) prepared under certain conditions of sputtering, in order to provide a plausible explanation for the relative inferiority of the photoresponse in all hydrogenated binary systems. Further, hypotheses will be made which are capable of explaining the smaller reduction of pseudogap density of states in a-Ge:H than in a-Si:H. Finally, the underlying reasons for the variability in the efficacy of H incorporation will be used to suggest possible improvements in the method of compensating defects.

Codeposited samples of a-$\mathrm{Si}_{1-x}\mathrm{Ge}_x$:H of different x were prepared on (cathode) substrates of Corning 7059 glass, c-Si, and quartz held at 100 or 250 °C. The total pressure of $GeH_4 + SiH_4$ was kept constant from run to run, with the result that the rate of deposition, for the same applied power, increased monotonically with x from 0.1 μm/min for $x = 0$ to 0.5 μm/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 O less than 0.5% and C less than 0.1%. No Si-O infrared vibrational absorption was observed, even in films 12 μm thick. SIMS also confirmed uniform depth profiles of H, Si, and Ge. Transmission-electron-microscopy (TEM) and secondary-electron-microscopy (SEM) micrographs showed smooth, homogeneous regions with no evidence of columnar growth in the magnification range available, but this does not in itself guarantee the absence of heterogeneity on a scale less than about 100 Å. Although many optical and transport measurements have been completed which give the familiar signatures of H incorporation and provide evidence on the alteration of pseudogap density of states, we shall concentrate here on experiments bearing on the structure and chemistry: the evolution of H on heating, the infrared vibrational absorption spectra, and the remeasurement of these spectra at various stages of anneal.

Figure 1 shows evolution spectra for samples of different x. Whereas a large fraction of the H evolves from Ge near 150 °C, the evolution from Si occurs above 400 °C. The spectra for the alloys are intermediate, generally resembling the spectrum of the dominant component. We deduce that, for this series of preparations, Ge and Ge-rich alloys contain weakly bonded H in configurations unidentified so far. From the total pressure produced when all the H has been evolved, the volume of the container, and the mass of the sample, we can obtain the atomic fraction of H. These are shown in Table I. It appears that the alloys contain more H than the end elements.

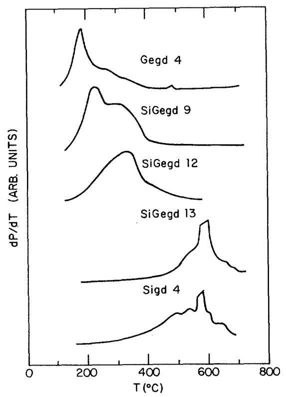

FIG. 1. Evolution of H from a-$Si_{1-x}Ge_x$:H alloys.

The infrared spectra were measured in the as-deposited condition and after successive anneals at several temperatures. Representative examples are shown in Fig. 2. The integrated area under the wag mode near 600 cm^{-1} has been used to obtain the content of bonded H, by assuming the (equal) matrix elements for absorption by Si-H and Ge-H wag modes determined with use of H contents derived from the nuclear-reaction method.[4] This H content, H_{ir}, is less than that found by evolution, H_{ev}, which is itself (because of H diffusion into the quartz of the evolution chamber) a lower bound on the total H content. Despite problems involved in transferring an empirical calibration on matrix elements between laboratories, it appears that the increase in $(H_{ev} - H_{ir})/H_{ir}$ as the Ge content is increased suggests the existence in a-Ge:H and a-Ge-rich alloys of weakly bonded H.

Unalloyed Ge:H shows absorption features assigned to stretch modes at 1875 and 1975 cm^{-1}. The corresponding modes for Si:H occur at 2000 and 2090 cm^{-1}. To estimate the fraction of hydrogen bonded to Ge and Si in the alloy SiGe:H, therefore, we fitted the observed absorption spec-

TABLE I. Characteristics of glow-discharge a-$Si_{1-x}Ge_x$:H alloys.

Sample	Composition (atomic %)			Preferential H Attachment, P
	Ge-content	H-content		
	Microprobe x	Evolution	IR Absorption Wag Mode	
GeGD-2	100	9	2.6	-
GeGD-4[a]	100	10	5.0	-
SiGeGD-1	90	-	3.2	10.5
SiGeGD-4	88	-	3.9	13.5
SiGeGD-9	82	18	9.4	13.0
SiGeGD-12[a]	70	38	23.0	9.7
SiGeGD-8	68	10	9.1	11.6
SiGeGD-14	65	13	9.5	10.3
SiGeGD-3	55	-	8.0	12.5
SiGeGD-2	42	-	11.4	10.4
SiGeGD-6	28	-	10.3	8.2
SiGeGD-7	26	-	12.0	14.0
SiGeGD-13	14	15	9.2	~ 20
SiGD-4	0	8	10.7	-
SiGD-10[a]	0	15	11.6	-

[a] Samples deposited at $T_S = 100$ °C; for all others $T_S = 250$ °C.

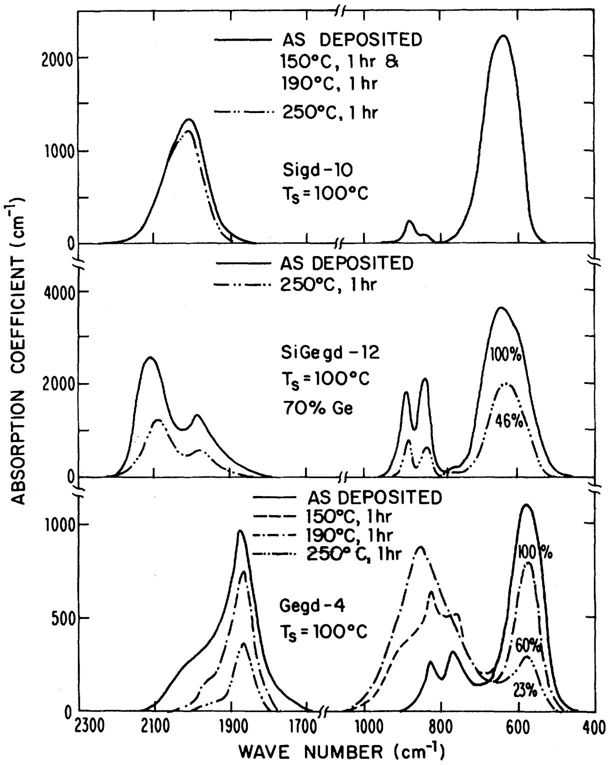

FIG. 2. Post-evolution annealing effects on ir absorption of a-$Si_{1-x}Ge_x$:H alloys.

trum to Gaussians centered at 1875, 1975, 2000, and 2090 cm^{-1}, assigning the lower two to Ge:H and the upper two to Si:H. In all alloys except SiGe sample GD-12 (Fig. 2) the contribution at 2090 cm^{-1} was quite small.

If we now evaluate the quantity

$$P \equiv \frac{\text{integrated Si-H absorption}}{\text{integrated Ge-H absorption}} \times \left[\frac{(\text{Si content})(\text{Si-H matrix element})}{(\text{Ge content})(\text{Ge-H matrix element})}\right]^{-1},$$

we get a measure of the preference (P) for H to bond to Si rather than to Ge. The relative Si/Ge contents are given by the microprobe analysis. The assumption that the relative matrix elements [1.9 (Ref. 4)] for absorption by Si-H and Ge-H individual bonds are not altered by changes in composition seems a reasonable approximation in view of the nearly equal electronegativities of the two elements. The preference ratio P, given in Table I, is uniformly of the order of 10, a result that has great significance for the properties of these and other binaries.

It might seem risky to deconvolute two features so close together as 1975 and 2000 cm^{-1}. Figure 3 illustrates that this deconvolution can be performed unambiguously. In practice, however, the best fits showed very little contribution from the 1975-cm^{-1} mode for any of the alloys; this higher Ge:H mode seems to disappear when Ge is alloyed with Si. We note that this mode also disappears when fluorine is added to GeH_4 during the deposition of Ge:(H, F) systems.

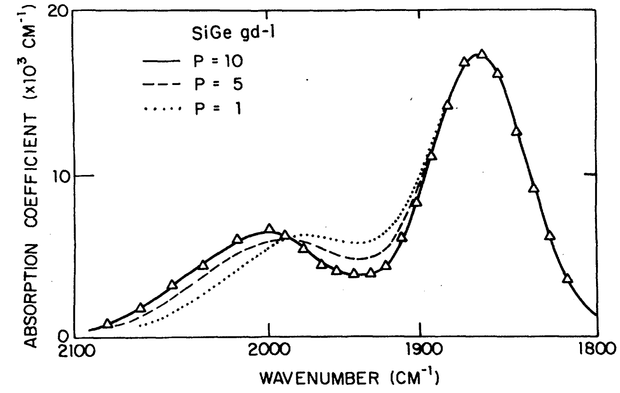

FIG. 3. Typical fits to the observed absorption features assigned to Ge:H and Si:H stretch modes. Triangles, observed absorption; solid line, fit to two Gaussians centered at 1875 and 2000 cm^{-1} (these fitted values yield a preference ratio $P = 10$); dashed line, fit forced to incorporate a contribution at 1975 cm^{-1} sufficient to reduce P to 5; dotted line, fit with the 1975-cm^{-1} component increased sufficiently to reduce P to 1.

Next we examine the changes in the spectra on anneal. For pure a-Si:H prepared at $T_s = 100$ or 250 °C, no H is evolved by 250 °C, and, consistent with this, there is no change in the infrared spectra. In contrast, annealing at 150 °C for 1 h of a-Ge:H prepared at 100 °C evolves a considerable amount of H (see Fig. 1), but there is no observed change in the stretch- and wag-mode regions of the infrared spectra. The same effect is present, although less marked, in the alloys. We conjecture that it is caused by the weakly bonded H in a-Ge:H and alloy films. The glow-discharge a-Si:H films of this study do not show this effect, but films sputtered under certain conditions do.[5-7] Finally, annealing leads to the observation of a broad Ge-O band (~ 860 cm^{-1}) in a-Ge:H, but not in any others. This is taken to reflect a difference in the microstructure of the Ge films from the Si-alloy ones.

We now put forward a tentative model for these observations, which originates in the generally observed heterostructure of films deposited from vapors, the particular observations on Si-H films produced by glow discharge,[8] and the confirmatory experience of our own laboratory in evaluating the transport and other properties of sputtered Si-H alloys.[3] In the latter case, we supposed that the Si films nucleated and grew in islands which eventually sought to join together, which led to a two-phase material of "islands" and "connective tissue" which were different in structure, chemical composition (H content), and electronic band structure.

In a-Si:H alloys we expect the H attachment to be sufficiently strong so that Si-H bonds on the surfaces of islands are preferred to reconstructed Si-Si bonds as the film grows. By contrast, we suggest that in a-Ge:H, the H attachment is weaker so that reconstructed Ge-Ge bonds often win out on the island surfaces. The connective tissue of Ge and Ge-rich alloys is postulated to be such that it contains a large density of defects and permits the trapping of H. This model is evidently consistent with the evolution of much weakly bonded H from Ge-rich alloys and with the details of the changes in infrared spectra on anneal.

The more effective removal of pseudogap states in a-Si, by H compensation of defects, over other amorphous semiconductors may now be rationalized. It has several ingredients:

(1) The preference ratio for H attachment to Si over Ge, a factor of 10, seems to be firmly established, given the argument that the ratio of matrix elements for absorption by Si-H and Ge-H bonds remains constant near the value determined in Ref. 4 as the composition x of $Si_{1-x}Ge_x$:H alloys changes. Such preferential attachment is not new in the amorphous semiconductor literature, since the same conclusion was reached earlier by a somewhat different combination of experiments on a-$Si_{1-x}C_x$:H.[9] We believe it to be a general effect possible in all hydrogenated binary systems. It implies that defects connected with one element of a binary may be left uncompensated while H substitutes for the other element, which would provide adequate reason for the poorer photoelectronic properties of all binary alloys with respect to the pure elements.

(2) Preferential attachment in a binary does not explain the inferior compensation of defects by H in a-Ge itself. Our hypothesis, which is less firmly based than that concerning preference, nevertheless has the same genesis: It is that the Ge-H bond is less strong with respect to its competitors in a growing film (reconstructed, long Ge-Ge bonds, for example) than is the Si-H bond with respect to *its* competitors. The end result is a different microstructure which experiment shows is more highly defected and contains relatively more weakly bonded H.

(3) It is a corollary to our postulates of relatively weak Ge-H bonding that a different compensator might more effectively reduce the dangling-bond density of a-Ge. It has been claimed that F possesses advantages in this regard over H in a-Si,[10] but in fact its substitution for H has not yet been shown to produce significantly different gap state densities or photoresponses. In the present context, however, the stronger F or O bond may well compete more effectively with alternatives in a-Ge. The incorporation of O would have the additional advantage that it could promote the joining of growth islands and so reduce the volume of defected connective tissue. Improvement of binaries by this device might nevertheless remain problematical if preferential attachment occurs for the new compensator. We are currently testing these ideas on Ge containing O and F.

Many factors must determine the photoelectronic properties of hydrogenated binaries. We have identified two, the preferential attachment of H to Si in SiGe and the probability of increased disorder/microstructure in Ge-rich material, as playing a role. It is still nevertheless possible that a judicious combination of deposition temperature and plasma composition may thwart the apparently deleterious effect of the two identified processes and yield usable device material.

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Measurement of Exciton Diffusion Lengths in Nd$_x$La$_{1-x}$P$_5$O$_{14}$ by Four-Wave Mixing Techniques

Christopher M. Lawson and Richard C. Powell
Physics Department, Oklahoma State University, Stillwater, Oklahoma 74078

and

Walter K. Zwicker
Philips Laboratories, Briarcliff Manor, New York 10510

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Transient four-wave mixing techniques have been used to measure the decay rate of the excited-state population grating in Nd$_x$La$_{1-x}$P$_5$O$_{14}$ samples as a function of grating spacing. The results show that at room temperature there is diffusive energy migration over distances of the order of 0.36 μm in the highly concentrated samples.

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Degenerate four-wave mixing (FWM) spectroscopy has been shown recently to be a powerful method for studying spatial migration without spectral transfer of electronic excitation energy in solids.[1-4] This technique has been used to determine the diffusion coefficient of molecular excitons in organic solids,[1] but attempts to make similar measurements on Frenkel excitons in inorganic materials have resulted only in placing an upper bound on the diffusion coefficient because the migration is too short to observe in the samples which have been studied.[2-4] We report here the results of FWM measurements on single crystals of Nd$_x$La$_{1-x}$P$_5$O$_{14}$ at room temperature. The presence of energy migration is easily observed and it is found to be diffusive with a migration distance of the order of 0.36 μm. These results are of significant importance since they represent an unambiguous determination of the range of energy migration in this class of stoichiometric materials used as "minilasers" for low-threshold, high-gain applications.[5,6] The mechanism causing concentration quenching of the fluorescence in these materials is not understood but it is known to have quite different properties from other neodymium laser materials.[5] This is not only an interesting fundamental physics question, but it is also important in material development for laser applications. The contribution of energy migration to concentration quenching in neodymium pentaphosphate has been the subject of significant interest and some controversy, with estimates of migration lengths ranging from a few angstroms to a few microns.[7-15] These FWM results provide an answer to one of the fundamental questions surrounding this controversy.

The samples used for this investigation were cleaved from high-quality single crystals grown by the technique described recently.[16] Several different experimental arrangements have been used to establish and probe population gratings of excited states. A schematic diagram of the setup used for this work is shown in Fig. 1. The 5145-Å line of an argon laser was used since it falls on one edge of a Nd^{3+} absorption line. The absorption of this light by the Nd^{3+} ions in the sample creates a spatial distribution of excited states with a sinusoidal pattern of wavelength $\Lambda \approx \lambda/\theta$, where θ is the crossing angle of the write beams and λ is the wavelength of the light in the sample. This "population grating" can cause the probe beam to be scattered with the maximum scattering efficiency occurring when the Bragg condition is satisfied.

Figure 2 shows the results from measuring the decay rate K of the scattered probe beam as a function of the square of the crossing angle of the write beams for single crystals of NdP$_5$O$_{14}$ and