ment that appears in the vicinity of 100 keV.

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Structure of Amorphous $(Ge, Si)_{1-x} Y_x$ Alloys

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I propose kinetically determined topological models of lightly doped ($x \leq 0.05$) amorphous (Ge, Si)_{1-x} Y_x alloys ($Y = H, F, B, P, \ldots$). Without adjustable parameters the model relates the lowest concentration $x_{\rm H}^0$ of hydrogen atoms required to quench paramagnetic dangling bonds to the concentration c_0 of unpaired spins at x = 0. Also discussed are the structural differences between freshly evaporated a-(Ge, Si) and various stages of ion-bombarded ("amorphized") crystalline material.

In the absence of definitive structural characterization by three-dimensional diffraction data, the most popular structural model for a-(Ge,Si) has been the infinite continuous covalent network with coordination number $N_{cn} = 4$. However, I have recently shown¹ that such networks, characterized by valence force field interactions, are strain free only for $\overline{N}_{cn} \leq 6^{1/2}$, and that with $N_{\rm cn}$ = 4 in order to be strain free such a network would have to be embedded in an $N_d = 8$ (eightdimensional) space. In the past it has been assumed that large excess strain energy (which renders the material amorphous rather than glassy) is accommodated entirely locally by equally admixing a fraction γ of five- and sevenmembered rings into the six-membered rings of the crystal.² The present model assumes that such diversification of the ring population exists but is insufficient to prevent the accumulation of strain energy of order $\alpha \gamma^2 \lambda^2$, where α is a bondstretching force constant such that bonds are broken intrinsically at characteristic spacings λ of order 20-40 Å. In the present topological

model, I do not calculate γ or λ from known interatomic forces and bond-breaking energies. However, I do obtain new relations between defect densities and I do predict novel kinetic effects in a material which is initially crystalline and is disordered systematically by ion bombardment.

Convincing evidence that internal surfaces exist and are intrinsic to a-(Ge,Si) has appeared slowly.³⁻⁷ To describe this evidence I adopt the following conventions. A broken bond is one which can be saturated by a monovalent element $Y_1 = H$ or F; the concentration of such bonds is $x = x_{H}$ $+x_{\rm F}$, and an atom with one (two) broken bonds is represented by Si* (Si**). The minimal concentrations in a fully disordered sample of surface, edge, and kink sites are represented, respectively, by x_s , x_e , and x_k . The contamination-free concentration of paramagnetic dangling bonds in similar samples is denoted by c_0 and its accepted value^{3,4} is $c_0 = (1 \pm 0.5) \times 10^{-3}$. The minimal concentration of hydrogen required to quench these spins is denoted by $x_{\rm H}^{0}$. Ordinarily heavy hydrogen doping $(0.1 \le x_{\rm H} \le 0.5)$ is used to quench the spins and remove trap states from the semiconducting energy gap.³⁻⁶ More recently evaporated *a*-Si films which have been subsequently heat treated in a hydrogen plasma have been shown⁷ to have many properties similar to those of heavily hydrogenated films, although *x* was only $x = x_{\rm H}^0 = (1 \pm 0.5) \times 0.035$.

The discrepancy in several orders of magnitude between c_0 and $x_{\rm H}^0$ has been most puzzling. Spear has even suggested⁴ that the quenching of paramagnetic spins by Y_1 = H may be an adventitious effect associated with preparation kinetics. I adopt the more traditional view that hydrogen has saturated the (intrinsically) broken bonds of the disordered, fully three-dimensional covalent network, and I utilize my topological model to reconcile c_0 and $x_{\rm H}^0$.

The crux of the model is that atoms with broken bonds, Si* and Si**, occur in arrays which are the dominant structural subunits. (Atoms with broken bonds may also occur in isolation, i.e., as point defects, but apparently these point defects have little effect on the accumulation of strain energy in over-constrained networks, and they in practice act only to obscure the intrinsic structural behavior.) The electronic structures of broken bonds in such arrays can be understood in terms of previously explored surface energy bands.⁸ A priori one might reason that Si* is paramagnetic (odd number of unpaired electrons) while Si** (even number of unpaired electrons) is nonmagnetic. Because of atomic relaxation (array reconstruction) exactly the reverse holds. as I now show.

The array of Si* atoms is equivalent to a freshly cleaved Si(111) surface, which is known to buckle (2×1) reconstruction. The nature of this reconstruction is well established⁸: Secondneighbor atoms form pairs with one Si* displaced outward gaining an electron to form a lone pair. the other Si* displaced inward losing its unpaired electron. A linear array of Si** atoms is similar to a line of second-neighbor atoms on a Si(100)surface. These dimerize, with attractive lateral instead of repulsive vertical displacements, so that each pair of (previously second-neighbor) Si** atoms shares a bond, leaving only one dangling (paramagnetic) bond per atom.⁸ This explains the paradoxical reversal noted above. Incidentally, this reversal could not easily be explained by a parametrized model which discussed only the electronic structure of isolated defects or bonds and proposed to treat the effects of

strongly repulsive or attractive atomic displacements by perturbation theory. Such an approach precludes level crossings, and in both the oneand two-broken-bond arrays it is the reconstructive level crossings that lead to the reversal in magnetic character. Moreover, these crossings occur just because the atoms with broken bonds occur in degenerate arrays on the surfaces of self-limited clusters.

To establish a relation between c_0 and $x_{\rm H}^0$, I assume that freshly evaporated material consists of self-limited clusters containing, on the average, \bar{N}_0 atoms. These clusters are connected by bridges which are important to the electrical properties⁹ and which provide surfaces for atomic diffusion between clusters. Apart from factors of order unity, the average numbers \bar{N}_s of surface atoms and \bar{N}_e of edge atoms per cluster are given by $\bar{N}_0^{2/3}$ and $\bar{N}_0^{1/3}$, respectively. Thus, $N_s^2 = N_0 N_e$ and we find

$$x_s^2 = x_e \,. \tag{1}$$

According to our earlier discussion, the Si* surface atoms are nonmagnetic and $x_s = x_{\rm H}^{0}$. However, the quasiplanar (111) cluster surfaces meet in cluster (100) edges containing Si** atoms, and these are magnetic; thus $x_e = c_0$. In observational terms Eq. (1) thus becomes

$$x_{\rm H}^{0} = c_0^{1/2}, \tag{2}$$

a relation which is very well satisfied by the experimental data. The crucial assumptions behind (1) and (2) are that the convexity of the cluster is concentrated entirely at quasilinear (100) edges between quasiplanar (111) pseudofaces and that we can separate $x_{\rm H}$ into its bulk component $x_{\rm H}^{b}$ and its surface component $x_{\rm H}^{0}$. This can be done either by plasma hydrogenation⁷ or by observing⁶ the concentration dependence of the stretching doublet GeH (surface sites) or GeH₂ (bulk sites) in infrared absorption; the surface component is narrow and saturates at $x_s = x_{\rm H}^{0}$. Finally, note that even if N_0 is uniformly distributed between limits which differ by a factor of 20, Eqs. (1) and (2) are changed by only 20%.

After hydrogenation a certain concentration x_T of trap sites still exists which is extremely sensitive to preparative procedures. The present model identifies x_T with x_k , the concentration of kinks along edges between quasiplanar cluster faces. At such kinks complete hydrogenation may be prevented by steric hindrance.

One of the objections which can be brought against the topological self-limited cluster model

(which is not to be confused with older polyhedral geometrical models⁹) is that a crystalline material which has been disordered by ion bombardment to saturation exhibits electronic properties indistinguishable from those of evaporated material.¹⁰ It is generally believed that ion bombardment produces vacancy-interstitial pairs, with the interstitials diffusing to external surfaces and the vacancies forming complexes which grow into microvoids (with diameters of order 5 Å or more). The key point kinetically is that if by bombarding to saturation we are augmenting the irregular set of microvoids with a system of (strain-relieving) interconnecting tunnels then the structure has developed one internal surface and has become topologically equivalent to selflimited clusters connected by bridges. The existence of a single internal strain-relieving surface is probably a prerequisite for successful subsequent plasma hydrogenation, but it is not necessary for hydrogenation by proton bombardment. There the nature [i.e., connectivity and "(111)ness"] of the internal surface can be monitored in a controlled way¹¹ by combining bombardment (both by Si and by H) with more conventional electron paramagnetic resonance, infrared, and optical absorption-edge experiments.

To extend our discussion of a-(Si, Ge) to materials doped with cations and anions we recall a basic principle of crystal chemistry, namely that atoms containing lone pairs prefer surface sites to bulk sites. The simplest illustration of this principle is the structure of layer $A^{III}B^{VI}$ compounds. Most physicists, when asked to choose between A-B-B-A and B-A-A-B structures for these materials, prefer the former (which contains no repulsive cation-cation contacts), but nature prefers the latter. Apparently the correlation energy of the (nearly free) lone-pair electrons is much greater when they are on the outside, and this overwhelms the cation-cation repulsion of the B-A-A-B configuration.

The present structural model has many implications; as examples I discuss some recent data¹² on Y_3 =B and P doping of sputtered hydrogenated *a*-Si. The P produces a deep (binding energy about 0.5 eV) impurity level which is broadened but still distinguishable as a peak in optical absorption. The optical absorption added by the B impurities is much broader and its only distinguishable feature is a change in slope, correponding to a binding energy of perhaps 0.8 eV. According to the present model, P should cover the threefold-coordinated sites of the surfaces of

the clusters; this is ordinarily called surface segregation. The observed peak could then be associated with surface states, which would explain why the binding energy is 0.5 eV, about three times larger than the binding estimated for isolated P impurities.^{12,13} The small B cations, on the other hand, are expected predominantly to occupy threefold-coordinated sites in cluster interiors, where their presence would reduce the strain energy. Many of these B sites will form clusters containing five to ten atoms, corresponding to fragments of boron or boron hybride molecules, and giving rise to the broad and nearly featureless observed optical absorption. I find this model more plausible than the assumption that both B and P occupy fourfold-coordinated bulk sites of amorphous material.

Another recent result which has attracted much interest is the report¹⁴ that fluorinated a-Si doped with donors has an electrical conductivity $\sim 10^2$ larger than comparably doped hydrogenated a-Si. The electrical properties of the present model are dominated by the conductivities of the bridges between clusters. The surfaces of these bridges are saturated equally well by fluorine or hydrogen and $x_s(\mathbf{F}) = 0.04 \cong 0.035 = x_s(\mathbf{H})$. However, **F** is much more electronegative than H, which means that electron space charge in the bridges will avoid F-covered surfaces much more than H-covered surfaces, thereby reducing surface scattering and trapping. If the cross-sectional areas of the bridges are $\leq (10 \text{ Å})^2$, this could have a very large effect on electrical conductivity.

Mathematically oriented theorists may be interested in the following observation. The present model ascribes the defect behavior of lightly doped a-(Si, Ge) to an intrinsic surface/volume ratio. Such an intrinsic ratio could be produced kinetically by diffusion of atoms via interconnecting bridges between clusters (the strain-relieving process alluded to above). This is a kind of percolation process, and there will be no strain just at the percolation threshold $p = p_c$. Now it is a characteristic of all large random clusters in lattice models that the ratio of number of surface atoms $n_s(p_c)$ to number of bulk atoms $n_b(p_c)$ is a constant.¹⁵ Because of the omission of van der Waals forces between nonbonded atoms, the lattice models yield unphysically large values of $n_s(p_c)/n_b(p_c)$ compared to the value ~ x_s ~ 0.03 appropriate to a-(Si, Ge), but the principle that $n_s/$ $n_b = \text{const}$ should hold even for more realistic models.

The reader's attention is drawn to two recent

theoretical papers on this subject, based on pointdefect (nontopological) models.^{16,17} I am grateful to W. Paul, G. A. N. Connell, M. H. Brodsky, and S. G. Kirkpatrick for discussions and preprints. D. R. Hamann suggested several improvements in exposition.

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Ultrahigh-Pressure Laser-Driven Shock-Wave Experiments in Aluminum

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We have measured the velocities of strong laser-driven shocks in aluminum. Pressures of 0.6 and 1.8 TPa were produced by incident laser intensities of 8×10^{13} and 3×10^{14} W/cm². This is the first time that pressures this high have been inferred in a laboratory experiment.

Present laboratory physics experiments are limited to pressures below about 0.5 TPa (1 TPa = 10 Mbar). To explore higher-pressure regimes, very large-scale experimental configurations, such as those employing nuclear explosives,^{1, 2} have been required in the past. Few experiments of this type have ever been performed because of their scale and cost. Since present theoretical calculations are reliable only above 10-100 TPa. there exists a large range of pressures over which little is known about material properties. Along the principal Hugoniot this pressure range

is of interest because temperature and pressure ionization effects, strongly controlled by atomic shell structure, may dominate many physical properties.

The capability of high-power lasers to produce ultrahigh shock pressures has been predicted for many years,³ and the success of present laser fusion research is indirect testimony to the validity of these predictions. However, the pressures reported in previous laser-driven shock studies⁴⁻⁶ have been much lower than those predicted theoretically. In this Letter we present the first di-