ground state must lie above the shallow donor levels ($E_D \sim 100$ meV), leading to an acceptor binding energy of $\gtrsim 3.3$ eV. Dietz et al.[5] have constructed detailed wave functions for the Cu^{++} ground state. To this information we now add a binding energy, and for the first time the ground-state wave function and binding energy of a very non−effective-mass-like deep center are available, and should prove invaluable in the discussion[4] of the origin of the binding energy of deep centers. Finally, we propose to extend the usual[9] symbolic representation of neutral and ionized impurities to include more specifically an acceptor with a tightly bound hole in the $3d$ shell. Thus we write the ground state (and excited d states) of the neutral copper acceptor as [+−].

In our model of the excited state the copper $3d$ shell is filled. A hole exists in the vicinity of the copper site (the excited state g factor is -2.36), although it is no longer in the highly shielded, localized level of the copper atom. From the energy of the transition (2.86 eV) and the lower limit of E_A (~ 3.3 eV) the excited state of the green emission lies ~ 450 meV above the valence band maximum, and in the effective-mass approximation[10] it will have a Bohr radius of ~ 2.4 Å. The hole is thus quite localized, even in the excited state. The latter is quite like the ground state of a simple neutral acceptor, i.e., no d shell holes but with a hole moving in the vicinity of the impurity. Hence this state may be represented by the usual neutral acceptor symbol, $\ominus^{+}$. A tight-binding[5,11] description would associate the excited-state hole with the four oxygen atoms surrounding the copper impurity (the average Zn-O band length is ~ 1.99 Å). The luminescence process is thus the transfer of a hole from an orbital encompassing these oxygen

atoms to a highly shielded, localized level of the copper atom.

This is the first detailed study of a transition between a highly shielded, localized level of an impurity and a level which is strongly perturbed by charge-transfer (valence band) states in a crystal. As such it provides new and important information about the detailed role of copper, and presumably other deep acceptors, in electronic processes in covalent semiconducting solids.

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[1]G. Heiland, E. Mollwo, and F. Stöckmann, Solid State Phys. 8, 191 (1959).

[2]Reference 1 summarizes the situation up to that time; for more recent proposals see D. Hahn and R. Nink, Physik Kondensierten Materie 4, 336 (1966); B. Andress, Z. Physik 170, 1 (1962); E. Mollwo, Z. Physik 162, 557 (1961).

[3]This work. T. Skettrup and L. R. Lidholt [Solid State Commun. 6, 589 (1968)] have reported qualitatively similar results.

[4]R. Dingle, to be published.

[5]R. E. Dietz, H. Kamimura, M. D. Sturge, and A. Yariv, Phys. Rev. 132, 1559 (1963).

[6]M. DeWit and T. L. Estle, Bull. Am. Phys. Soc. 8, 24 (1963).

[7]Attempts to prove this point, using isotopically enriched crystals, have not yet been successful. This is attributed to strain broadening of the no-phonon pair.

[8]The g factors recently reported [R. Dingle, Bull. Am. Phys. Soc. 13, 1476 (1968)] require revision.

[9]M. A. Lampert, Phys. Rev. Letters 1, 450 (1958). A modification has been necessary for the case in which two signs would be enclosed in the circle.

[10]W. Kohn, Solid State Phys. 5, 257 (1957).

[11]C. A. Coulsen and M. J. Kearsley, Proc. Roy. Soc. (London), Ser. A 241, 433 (1957).

ELECTRON SPIN RESONANCE IN AMORPHOUS SILICON, GERMANIUM, AND SILICON CARBIDE

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The g values, line shapes, and linewidths of the ESR signals from within the bulk of amorphous silicon, germanium, and silicon carbide are found to be similar to those of the electron states observed in the surface regions of the corresponding crystalline forms. Discussion is given in terms of a microcrystalline model.

We report the measurement and identification of the ESR signals in thin films of amorphous silicon, germanium, and silicon carbide. The g values, line shapes, and linewidths of the spin-

resonance signals are found to be similar to those of the electron states observed in the surface regions of the corresponding crystalline forms. However, in the amorphous films, the

strength of the signal is proportional to film thickness, indicating that the states are distributed throughout the bulk of the material. Annealing studies have shown that the changes in the number of electronic states observed by ESR in amorphous Si are correlated with similar changes in electrical conductivity and optical absorption.[1] The density of spins observed for samples prepared and annealed near room temperature is of the order of 10^{20} spins cm^{-3} for all three of the semiconductors examined.

These results are relevant to the important unresolved problem of the structural arrangement of the amorphous phase. Two different viewpoints of the structure are the continuous-random-network and the microcrystalline models. Experiments have been unable to differentiate between these models by the conventional structural analysis techniques of x-ray and electron diffraction.[2] However, diffraction does give significant information about the short-range order of amorphous solids. The short-range tetrahedral ordering of the diamond lattice has been observed in the solid amorphous forms of Si[3] and Ge.[4] These amorphous materials have been referred to as having a latticelike structure[5] rather than the structure of molten Si[3] and Ge[4] or the liquid-like structure of solid amorphous Bi, Fe, and Ga.[6] The manner in which the short-range lattice structures are interconnected is not definitively known. ESR has been used here to give additional information concerning the structural nature of amorphous Si, Ge, and SiC. Amorphous semiconducting Si proved particularly suitable for study because of the wealth of information available about the ESR signals of single-crystal Si. This has permitted identification of the states responsible for the ESR in amorphous Si. Similar arguments apply to the ESR in amorphous Ge and SiC, whose semiconducting and structural properties are much like those of amorphous Si.[7]

The samples were prepared by rf sputtering of nominally undoped Si, Ge, or SiC cathodes onto water-cooled sapphire substrates. We found essentially the same results for an evaportated Si film. The samples were stored in air at room temperature between measurements and between isochronal high-temperature anneals. Each sample was identified as amorphous by x-ray or electron-beam diffraction. No changes in the diffraction patterns were observed for annealing temperatures below the crystallization temperature. The electron spin resonances were measured with the samples immersed in liquid nitrogen using an X-band microwave spectrometer. The number of spins was measured by comparison with a known amount of diphenyl picryl hydrazyl (DPPH). The accuracy of the determination of the signal intensity was $\pm 10\%$ and was limited by the reproducibility of successive insertions of the samples into the microwave cavity. The g factor of the signal was determined from a comparison with a laboratory standard of Mn^{2+} ions in a powdered SrS host whose spectrum brackets the signals of the samples.

Table I contains a summary of our results for the g values, linewidths, and density of spins observed for Si, Ge, and SiC. The resonant lines were symmetrical, Lorentzian, and isotropic. The densities of spins listed in the table were estimated from $N_S \propto CIW_H^2/W_{mod}$ for both the films and the DPPH standard. Here N_S is the total number of spins that contribute to a signal with a peak-to-peak height I and width W_H. W_{mod} is the width of the modulation magnetic field and C is a constant which is 1.81 for a Lorentzian line and 1.1 for DPPH.[8] For Si the linewidth was 7.5 G at room temperature and narrowed to 4.7 G at 77 and 4.2°K. The Lorentzian shape is indicative of either exchange or motional narrowing.[9] Such narrowing is strong evidence that the electrons are not localized at one site. The linewidths and g values did not change with annealing.

Also listed in the table are the similar g values and linewidths observed by Walters and Estle[10] in the surface region of the corresponding crystal phases. Walters and Estle had attributed the resonances to mechanically damaged regions below the crystal surfaces. However, in more recent work, Haneman[11] has shown that the same resonance occurs on clean cleaved Si surfaces. He identifies the unpaired electrons as being in s-type states which result from "dangling bonds" on the single-crystal surface. Furthermore, Haneman, Chung, and Taloni[12] observed that the mechanically damaged (e.g., polished) surfaces show the same resonance because of increased surface areas resulting from mechanical treatments. Although the amorphous films show surfacelike resonances we observe the same number of spins per unit volume regardless of film thickness. We have tested this on Si films from 0.3 to 5 μm thick and Ge films from 2 to 13 μm thick. All of the SiC films were 0.25 μm thick.

We identify the resonances observed in the amorphous Si, Ge, and SiC films as the same as those seen on the corresponding crystal surfaces

Table I. The ESR results on amorphous films compared with the results from similar resonances in crystalline material.

| Material | Amorphous films (77°K) (this work) | | | Other authors | | | | | | |
| | g value | Linewidth (G) | Density of spins[d] (cm^{-3}) | Amorphous films | | Crystalline surfaces | | Neutron irradiated crystals | |
				g value	Linewidth (G)	g value	Linewidth (G)	g value	Linewidth (G)
Si	2.0055 ±0.0005	4.7	2×10^{20}	2.006 ±0.001[c]	15[c]	2.0055 ±0.002[a] 2.0055[b]	7-8[a] 5[b]	2.0055[a]	16-20[a]
Ge	2.021 ±0.001	39	1×10^{20}			2.023 ±0.003[a]	50[a]		
SiC	2.003 ±0.001	6	3×10^{20}			2.0027 ±0.002[a]	5.5[a]		

[a]G. K. Walters and T. L. Estle, J. Appl. Phys. 32, 1854 (1961).

[b]D. Haneman, Phys. Rev. 170, 705 (1968).

[c]Z. Z. Ditina, L. P. Strakhov, and H. H. Helms, Fiz. i Tekh. Poluprov. 2, 1199 (1968) [translation: Soviet Phys. —Semicond. 2, 1006 (1969)].

[d]The densities are estimated to be accurate within a factor of 2.

rather than those of any other bulk defects observed in these crystals. For example, one cannot identify these defects with any of the vacancy or vacancy-impurity defects that are produced by electron irradiation of silicon.[13] The resonance signals of these bulk crystal defects are all anisotropic. None of the g values nor their averages $\frac{1}{3}(g_1 + g_2 + g_3)$ agree with the $g = 2.0055$ observed for the defects in amorphous Si. If any of these defects were present in the amorphous material their resonance lines would span the range of g values among g_1, g_2, and g_3 and produce an asymmetric line, wider than the observed amorphous line. (The line shape of an anisotropic signal in a polycrystalline or glassy material has been derived by Bleaney[14] and by Sands[15] and shown to be asymmetrical.) In addition, the resonance signals in the amorphous films cannot be identified with any of the usual donors or acceptors in these semiconductors since these require liquid-helium temperatures for observation by spin resonance.[16] Furthermore, none of the impurities[16] that have so far been observed by spin resonance has a spectrum comparable with that of the amorphous films.

We are therefore led to the conclusion that the defects that are observed in the amorphous films are similar only to those observed in freshly cleaved Si[10] surfaces or mechanically damaged crystalline surfaces of Si, Ge, and SiC.[11,12]

Recently Ditina, Strakhov, and Helms[17] have observed spin-resonance signals of defects in evaporated amorphous Si; however, they claim to have observed a new defect and not the surface states reported by Walters and Estle.[8] The g value of the signal, the concentration of defects (2 $\times 10^{20}$ cm^{-3}) and the fact that the number of defects scales with film thickness are all consistent with our observations. The linewidth of 15 G that they observed and the slight asymmetry of their line differs significantly from our data. The differences may be due to the different methods of preparation. For example, in neutron-irradiated Si, Walters and Estle[10] observed a resonance similar to that of the surface states but with a linewidth of 15-20 G. They attributed the differences in linewidths to the differences in the conditions under which the damage is produced. As pointed out above, the lines are narrowed by exchange or motional narrowing. Therefore the linewidth will depend on the degree to which the narrowing mechanism can act. This in turn may depend on such conditions of sample preparation as the size of the microscopic surface area around the defect.

The main significance of the above results is that electronic states characteristic of the crystal surfaces of Si, Ge, and SiC are observed to be distributed throughout the bulk of the amorphous forms of the same materials. The large density of these states makes it reasonable that they contribute significantly to other properties such as electrical conductivity and optical absorption. That this is the case is supported by

annealing studies on amorphous Si which show irreversible decreases in the electrical conductivity, optical absorption, and magnitude of ESR signal for isochronal anneals between room temperature and 500°C.[1] In addition, from the change in conductivity induced by an adsorbed oxygen layer on the surface of a 2400-Å-thick evaporated Si film, we estimate that there are about 10^{20} charge carriers per cm^3. These observations on annealing and the effect of surface charge lead us to believe that the states observed in the ESR experiment are responsible for important aspects of the electrical and optical behavior.

One possible model for these latticelike amorphous semiconductors is an aggregate of closely packed microcrystallites. Each crystallite can have "dangling bonds" which contribute to the electrical properties. It is not yet clear whether they contribute by providing carriers, sites, or regions of reduced potential barriers for a conduction process between crystallites. Evidence for structurally dependent conduction in amorphous Si and Ge had been pointed out by Walley[18] when he noted that the electrical conductivities and their temperature dependences were virtually the same for both materials. If the x-ray diffraction patterns of amorphous Si, Ge, and SiC are interpreted as indicative of crystallite sizes with linear dimensions of 10-15 Å,[19] then for a spin density of 2×10^{20} cm^{-3}, every second microcrystallite has a "dangling bond." Annealing reduces the number of "dangling bonds" and therefore the conductivity and ESR signal. Samples deposited and measured at lower temperatures show higher initial room-temperature conductivities and therefore presumably have more unbonded electrons at the microcrystalline surfaces. The effects of small crystallites and "dangling bonds" on the optical properties is not easily calculable. One effect is the relaxation on the selection rules for optical transitions which is probably responsible for the observed high absorption constants.[1,7] The large surface area and "dangling bonds" should cause strain and field effects on the fundamental absorption edge and may very from sample to sample because of growth and thermal histories.[1,20]

We have noted for heating cycles up to about 500°C[1] that the electrical, optical, and ESR properties of amorphous Si change gradually, but at a temperature near or above 500°C amorphous Si undergoes a crystallization transition accompanied by significant changes in all three properties. Amorphous Ge and SiC crystallize at a low-

er and higher temperature, respectively.[7] These structural changes are occurring at a temperature at which the surface atoms of the microcrystallites have enough mobility to rearrange and interact with neighboring microcrystallites. This view is consistent with ESR[9,10] and low-energy electron-diffraction[21] observations on single-crystal Si of the cleaved-to-annealed surface transformation in the temperature range 500-600°C. Single-crystal Ge surfaces undergo a similar transformation around 200°C.[21] Comparable data on SiC surfaces do not appear to be available.

In summary, we have observed by ESR a large density of electronic states in amorphous Si, Ge, and SiC which are identified as the same states occurring in the surface regions of the corresponding crystals. The results in conjunction with x-ray and electron-diffraction observations are interpretable in terms of a microcrystalline model for these group IVA latticelike amorphous semiconductors. The microcrystallites are stable in size, while "dangling bond" surface states gradually anneal out with increasing temperature until a temperature sufficient for normal crystallite formation is attained.

[1]M. H. Brodsky, K. Weiser, G. D. Pettit, and R. S. Title, Bull. Am. Phys. Soc. 14, 311 (1969), and to be published.

[2]A. Bienenstock and B. G. Bagley, J. Appl. Phys. 37, 4840 (1966); R. W. James, The Optical Principles of the Diffraction of X-Rays (Cornell University Press, Ithaca, N. Y., 1965), Chap. X.

[3]H. Richter and G. Breitling, Z. Naturforsch. 13a, 988 (1958).

[4]H. Richter and O. Fürst, Z. Naturforsch. 6a, 38 (1951).

[5]G. Breitling, in Proceedings of the International Conference on Thin Films, Boston, Mass., 1969 (to be published).

[6]H. Richter, in Proceedings of the International Conference on Thin Films, Boston, Mass., 1969 (to be published).

[7]R. Grigorovici, Mater. Res. Bull. 3, 13 (1968); J. Tauc, Mater. Res. Bull. 3, 37 (1968); A. H. Clark, Phys. Rev. 154, 750 (1967); C. J. Mogag and W. D.

Kingery, J. Appl. Phys. 39, 3640 (1968).

[8]Varian Associates, Inc., EPR Manual No. 87-100-074 (unpublished), p. 5-11.

[9]P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 23, 269 (1953); J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[10]G. K. Walters and T. L. Estle, J. Appl. Phys. 32, 1854 (1961).

[11]D. Haneman, Phys. Rev. 170, 705 (1968).

[12]D. Haneman, M. F. Chung, and A. Taloni, Phys. Rev. 170, 719 (1968).

[13]G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. 31, 86 (1961).

[14]B. Bleaney, Proc. Phys. Soc. (London) A63, 407

(1950).

[15]R. H. Sands, Phys. Rev. 99, 1222 (1955).

[16]G. W. Ludwig and H. H. Woodbury, Solid State Phys. 13, 223 (1962).

[17]Z. Z. Ditina, L. P. Strakhov, and H. H. Helms, Fiz. i Tekh. Poluprov. 2, 1199 (1968) [translation: Soviet Phys.—Semicond. 2, 1006 (1969)].

[18]P. A. Walley, Thin Solid Films 2, 327 (1968).

[19]T. B. Light and C. N. J. Wagner, J. Appl. Cryst. 1, 199 (1968).

[20]T. M. Donovan, W. E. Spicer, and J. M. Bennett, Phys. Rev. Letters 22, 1058 (1969).

[21]J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963).

ELECTRON MOBILITY TRANSITION IN A RANDOM SYSTEM OF HARD-CORE SCATTERERS*

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The mobility of an electron in an infinite system of randomly located identical hard-core scatterers is calculated to all orders in the density of scatterers. For fixed temperature a large drop in mobility is found at a characteristic density. The possible relevance of this result to the switching effect observed in amorphous semiconductors and the metal-insulator transition in a noncrystalline system is discussed.

The physics of systems displaying randomness in an essential characteristic is currently receiving considerable attention. The effect of randomness is presumed to be a common feature in numerous materials demonstrating metal-insulator transitions.[1] In theoretical investigations of electron transport, the introduction of a random potential at each site in the tight-binding model of a regular crystalline array leads to the Anderson transition.[2] Similarly, the presence of random fluctuations of charge density is responsible for the Mott transition when Coulombic interactions are involved.[3]

Transport in the presence of numerous identical scattering centers with randomness appearing in the spatial distribution has also been considered. Various authors have made quantum-transport calculations in the one-electron approximation. More recently, progress has been made on the problem of a system of interacting fermions.[4] All these theories consider a weak interaction and perform an expansion in powers of the strength of the interaction. The results are generally shown to be equivalent to those of

the quantum Boltzmann equation in lowest order, with various corrections arising in succeeding orders of the expansion.

In this Letter we report the results of a mobility calculation in which a switching effect appears for an electron moving through a system of identical randomly distributed scattering centers. The Kubo[5] quantum-mechanical response formalism was used in the limits of weak uniform external field and s-wave (low-energy, spherically symmetric) scattering. An earlier paper[6] presented the lowest order work in which we derived the relaxation time τ characterizing the system and a mobility which showed a slight drop below the results of the semiclassical Langevin theory.[7] With the present extension of the work to all orders in the density two distinct changes are noted. A shift occurs in τ and, at constant temperature, the mobility shows a severe change of many orders of magnitude for a correspondingly small change in the density. In the language of Mott,[8] this is presumably caused by the appearance of localized electronic states.

For a weak external electric field in the z di-