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CHEMICAL BONDING OF ALLOY AND DOPANT ATOMS IN AMORPHOUS SILICON

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Abstract.- The chemical bonding environments of Si and dopant atoms in alloys of a-Si are characterized through a local electronegativity. This parameter is used as a scaling variable for empirical relations based on molecular data: the chemical shifts in the frequencies of Si-H and Si-F local vibrations, and in the binding energies of Si 2p core states.

Introduction.- The frequencies of Si-H bond-stretching vibrations in silane molecules scale with the sum of the electronegativities of the other three atoms or groups (R_j as in Fig. 1(a)) bonded to the Si-atom (1). By isolating a local five-atom cluster, similar relationships have been shown to apply for both Si-H and Si-F vibrations in an a-Si host (1, 2). This paper improves the model by incorporating the properties of the host amorphous solid in a more satisfactory and quantitative manner. The model introduces the concept of a local electronegativity, defined at each atom site and determined primarily by its immediate neighbors, but also including the average properties of the host network. This procedure for calculating a local electronegativity is an extension of an approach previously applied to calculations of the chemical shifts of core-state binding energies in molecules (3). This paper applies a chemical bonding approach to calculations of the frequencies of Si-H and Si-F bond-stretching vibrations; the binding energies (B.E.) of Si 2p core states in a-Si,C and a-Si,F alloys; and the local electronic properties of donor atoms in a-Si.

Network Calculations.- The calculation of a local electronegativity, X_R^i , is based on an extension of the general principle of electronegativity equilization (5, 6). We use the electronegativity scale of Sanderson (5), noting that it is formally equivalent to the scales of Allred-Rochow (6) and Mulliken-Jaffe (6). In the Model of Ref. 5, the electronegativity, \bar{X} , of the two atoms of a diatomic molecule in their combined state is taken as the geometric mean of their atomic electronegativities, $\bar{X} = (X_{R1} X_{R2})^{1/2}$. The partial charges on each atom, e_{R1} and e_{R2} , are determined by the difference between this molecular electronegativity and that of the neutral atom. Extension of this procedure to polyatomic molecules yields the result that all atoms of a large molecule attain a common value of electronegativity; i.e., the geometric mean of the electronegativities of the constituent atoms. This is in conflict with XPS (or ESCA) results which indicate that the chemical shifts of atoms in large molecules reflect their immediate local chemical environment with smaller contributions due to more remote neighbors (3). A modification of the Sanderson approach that takes this into account has been developed (3) and applied to a variety of molecules (3, 4).

We have further extended this calculation, and have developed a procedure for calculating the local electronegativity of an atom, X_R^i , in an amorphous solid. Consider the Si-H or Si-F sites in an a-Si host, Fig. 1(b), or an a-SiO₂ host, Fig. 1(c). The procedure for calculating X_R^i for the Si-atom bonded to the H or F-atom is illustrated in Figs. 1(d) and 1(e). We construct a "molecule" consisting of the Si-atom and its immediate neighbors, the H or F-atom, and the three atoms labelled N_1 , N_2 and N_3 . To each of these N_j atoms we attach n_j pseudo-atoms, M, which have the mean electronegativity of the host. For a-Si, $n_j = 3$ and M has an

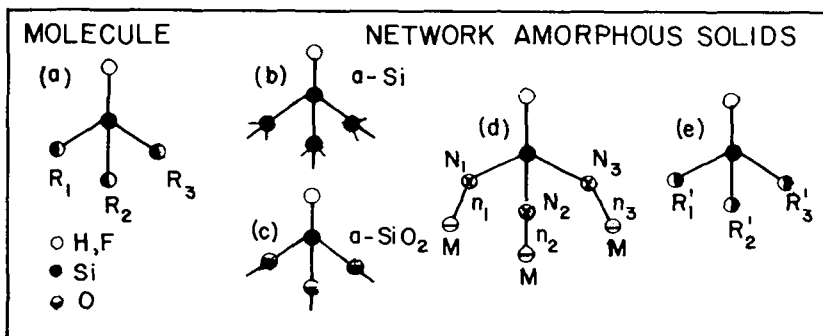


Fig. 1 Local atomic structure is (a) silane molecules, (b), (c), (d) and (e) network amorphous solids.

electronegativity, X_m , equal to that of a Si-atom; for a-SiO₂, $n_j = 1$ and $X_m = [X_{Si}X_O^2]^{1/3}$, the molecular electronegativity of SiO₂. We then apply the procedure discussed in Ref. 3, by combining the n_j M-atoms with their N_j neighbors. This yields a pseudo-atom, R_j^1 with $X_{R_j^1} = [X_M^{n_j} X_{N_j}]^{1/(n_j+1)}$. The local electronegativity of the Si-atom, X_{Si}^1 is then calculated in the usual way (6), i.e.,

$$X_{Si}^1 = (X_{R_1}^1 X_{R_2}^1 X_{R_3}^1 X_{Si} X_X)^{1/5} \quad (1)$$

where $X = F$ or H . This approach emphasizes the contributions of the immediate neighbors, but also includes through the definition of $X_{R_j}^1$ the properties of the host network.

Local Vibrations of Si-H and Si-F.— In previous publications (1, 2) it has been shown that the frequencies of Si-H or Si-F bond-stretching vibrations, $\nu(\text{Si-X})$, can be expressed in either of two ways:

$$\nu(\text{Si-X}) = \nu_0 + a_0 \sum X_{R_j} \quad \text{or} \quad \nu(\text{Si-X}) = \nu_0' + a_0' e_{Si} \quad (2)$$

where the coefficients ν_0 , a_0 or ν_0' , a_0' are determined by a linear regression analysis of molecular data. Since e_{Si} is proportional to the local electronegativity of the Si-atom, $e_{Si} = (X_{Si}^1 - X_{Si})/2.08 [X_{Si}]^{1/2}$, Eq. (3) can be recast with X_{Si}^1 as the chemical bonding variable, so that

$$\nu(\text{Si-H}) = 1433.2 + 199.5 X_{Si}^1 \pm 12 \text{ cm}^{-1} \quad \text{and} \quad \nu(\text{Si-F}) = 573.1 + 80.0 X_{Si}^1 \pm 11 \text{ cm}^{-1} \quad (3)$$

Fig. 2 includes these empirical relations as well as the frequencies of Si-X groups in a-Si, a-Si₃N₄ and a-SiO₂ hosts.* Similar types of regression analyses have been performed for the other groups; e.g., Si-H₂ and Si-H₃ (1, 2). These calculations yield assignments for modes that have been subject to some controversy; the 845 cm⁻¹ mode in a-Si:H is assigned as a wagging vibration of the SiH₂ group in a polysilane, (SiH₂)_n chain-segment, and of the 1015 cm⁻¹ mode in a-Si:F as a stretching vibration of an SiF₂ group in a similar (SiF₂)_n segment.

Chemical Shifts in Si 2p Core States.— The positions of atomic core states in molecules or solids reflect the local chemistry. The general approach is to include two contributions to the chemical shift of the core state of a given atom; one due to changes in its partial charge, and the second due to changes in the local electric field produced by the other neighboring atoms (3). It is however impossible to separate these two contributions via any experimental measurement. Our approach for calculating a local electronegativity implicitly includes both of these contributions and therefore is an appropriate scaling variable. In this context we expect changes in the bonding energy to correlate directly with changes in the value of X_{Si}^1 . This is indeed the case and for the binding energies (B.E.) of Si 2p core states, we obtain

$$\text{B.E.} = 89.7 + 3.25 X_{Si}^1 \pm 0.07 \text{ eV.} \quad (4)$$

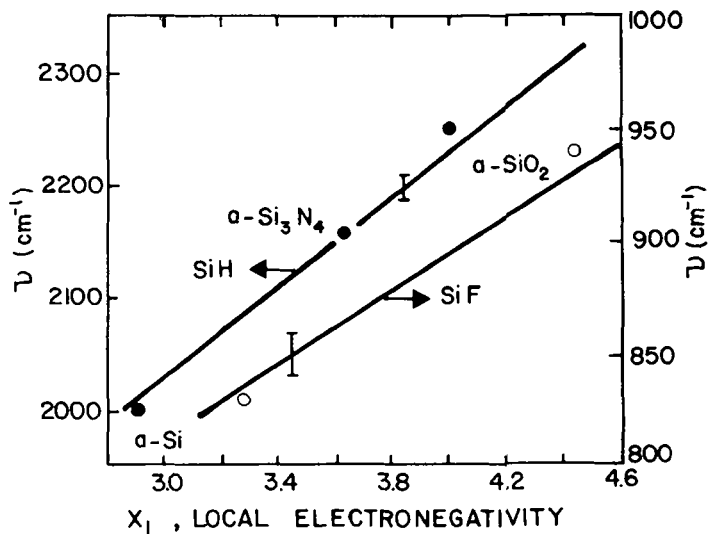


Fig. 2 Frequencies of SiH and SiF bond-stretching vibrations as a function of X_l . The solid lines are a linear regression analysis of molecular data. The points are experimental data for amorphous hosts.

Fig. 3 illustrates the application of Eq. (4) to a calculation of the B.E. of the Si 2p state in a-Si,C alloys (7). We assume a "virtual crystal" model in which the neighbors of a given Si-atom have the properties of an average alloy atom. The experimental results are well-described by this model; i.e., the chemical shifts of the B.E. of the Si 2p state are proportional to changes in the local electronegativity of the Si atom. XPS spectra have also been obtained for a-Si,H alloys (10). These studies indicate a chemical shift of approximately 0.15 eV for 10-15 atomic % H. Our calculations yield a similar value for the chemical shift.

The XPS spectra of a-Si,F alloys containing 30-40 atomic % F exhibit two features due to Si 2p states (8,9), one at about 99 eV attributed to Si-atoms with only Si-nearest neighbors and a second weaker feature at ~ 102 eV attributed to Si-atoms with more than one F neighbor, i.e., either SiF₂ or SiF₃ groups. In the context of model calculations based on Eq. (4) the peak at ~ 99 eV is due to Si-atoms

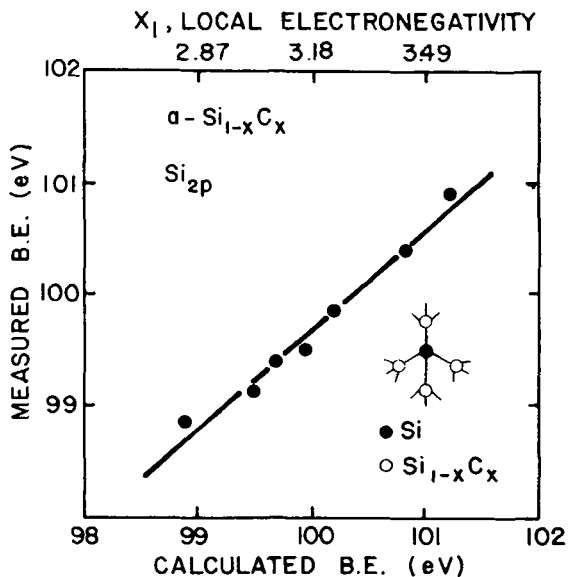


Fig. 3 Measured versus calculated B.E. for Si 2p core states in a-Si,C. The insert represents the "virtual-crystal" model used in the calculation.

with Si-nearest neighbors immersed in a host network with the average Si-F alloy properties. The peak at ~ 102 eV is best explained as being due to Si-atoms within $(\text{SiF}_2)_n$ groups. This interpretation of the XPS data is in accord with the interpretation we have given to the IR data; i.e., the feature at 1015 cm^{-1} . Other explanations have been proposed for these features, e.g., they are both due to SiF_3 (12); however, these explanations are not as well supported by our calculations.

Donor Atoms in a-Si.— There is a general belief that a-Si, doped with phosphorous or arsenic, contains two types of P or As-atoms; threefold-coordinated sites which are inactive as dopants, and fourfold-coordinated sites which are the analogs of the active donor-atom sites in crystalline-Si. There is also experimental evidence that doping by P or As can only be accomplished in the presence of H or F which remove defect states from the gap. This means that the three or fourfold-coordination by itself is not sufficient to promote doping. We have calculated a local electronegativity for the three and fourfold-coordinated sites of P in a-Si, and have used these values of X_p^1 to obtain the partial charges on the P-atom and its immediate Si-neighbors, and the B.E. of the P 2p core states. For the neutral P-atom in the threefold-coordinated site, $e_p = -0.12e$ and $e_{si} = +0.04e$. For the "positively" charged P-atom in the fourfold-coordinated site, $e_p \approx 0.0$ and $e_{si} = 0.17e$. The P 2p binding energies for these configurations are E.B. = -129.4 eV for P_3° and E.B. = -130.9 eV for P_4^+ . Preliminary XPS measurements on partially crystallized and heavily P-doped a-Si film yield an asymmetric line with two gaussian components at approximately 129 and 130 eV.

The negative partial charge on the P-atom in the P_3° inactive site may be the hole trap responsible for the enhanced electron photoconductivity in P-doped a-Si (11). This assignment assumes that P_3° and P_4^+ centers are introduced at all doping levels. A second model for the hole trap is that it is a native defect of the a-Si host; e.g., a threefold-coordinated and negatively-charged Si-atom, Si_3^- . This trap would then be activated by the movement of the Fermi level that accompanies the doping process. Furthermore, the trap in question would have not been neutralized by the univalent alloy constituent, H or F. This second model seems unlikely. Moreover, a similar argument to the one we have proposed above can also be invoked to explain the decrease of electron photoconductivity in Boron doped Si. This model is based on B_4^- active doping sites and B_3° inactive sites.

Summary.— We have developed a new method for calculating the local electronegativity for atoms in amorphous solids. We have shown that changes in this electronegativity can be used to explain changes in the frequencies of bond-stretching vibrations of Si-H and Si-F groups, and changes in the B.E. of the Si 2p core state. We have also demonstrated how the model can be used to identify differences in the local environments of three and fourfold-coordinated donor atom sites. A similar analysis is also applicable for acceptors.

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References.

- (1) LUCOVSKY G., *Solid State Commun.* 29 (1979) 571.
- (2) LUCOVSKY G., *A.I.P. Conf. Proc.* 73 (1981) 100.
- (3) CARVER J.C., GRAY R.C., and HERCULES D.M., *J. Amer. Chem. Soc.* 96 (1974) 6851.
- (4) GRAY R.C., CARVER J.C., and HERCULES D.M., *J. Electron. Spectrosc. Relat. Phenom.* 8 (1976) 343.
- (5) SANDERSON R.T., *Chemical Bonds and Bond Energy* (Academic Press, New York, 1971).
- (6) HUHEEY J.E., *Inorganic Chemistry*, 2nd Ed. (Harper and Row, New York, 1978).
- (7) USAMI K., SHIMADA T., and KATAYAMA Y., *Shinku* 23 (1980) 27.
- (8) SHIMADA T., and KATAYAMA Y., *J. Phys. Soc. Japan* 49 (1980) 1245.
- (9) LEY L., GRUNTZ K.J., and JOHNSON R.L., in Ref. 2, 161.
- (10) USAMI K., SHIMADA T., and KATAYAMA Y., *Jap. J. Appl. Phys.* 19 (1980) L389.
- (11) LECOMBER P.G., and SPEAR W.E., *Topics in Appl. Phys.* 36 (1979) 251.