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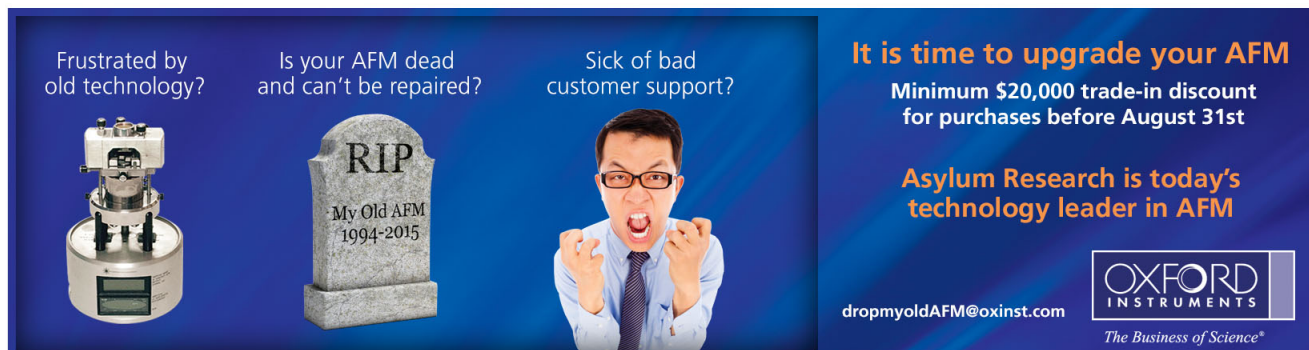
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Study of amorphous germanium-nitrogen alloys through x-ray photoelectron and Auger electron spectroscopies

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In this work, experimentally determined values of electron spectroscopic shifts induced by nitrogen in Ge core levels of substoichiometric amorphous germanium-nitrogen (*a*-GeN) alloys are discussed and presented. X-ray photoelectron spectroscopy (XPS) and x-ray excited Auger electron spectroscopy (XAES) are employed to study the behavior of the Ge *3d* and LMM spectra, respectively, and combined the corresponding XPS and Auger core levels shifts to determine $\Delta\alpha'$, the modified Auger parameter shift, which is exempt from problems inherent in the interpretation of XPS and XAES shifts. It is demonstrated how one can use $\Delta\alpha'$ to reliably estimate Δn_{Ge} , the change in Ge valence charge in the alloys, and how one can calibrate XPS shifts of Si and Ge based alloys in terms of approximate values of Δn_{Ge} . © 1995 American Institute of Physics.

This letter, reports the results of XPS (x-ray photoelectron spectroscopy) and XAES (x-ray excited Auger electron spectroscopy) studies of the effects of N atoms on the electronic levels of amorphous Ge. In particular, we show how $\Delta\alpha'$ can be used to estimate the change in valence charge of the photoexcited Ge atom in the alloy with a fair degree of reliability. The uncertainties intrinsic to the XPS and XAES shifts do not affect the Auger parameter. Furthermore, we illustrate an empirical linear relation between the XPS shift and $\Delta\alpha'$ in a wide range of compounds based on crystalline and amorphous Si and Ge networks, which permits an approximate calibration of Ge *3d* XPS shifts in terms of charge transferred upon alloying.

A detailed discussion on deposition conditions and on the structural and optoelectronic properties of the samples being reported here can be found elsewhere.¹ The XPS measurements were performed on Ar⁺ cleaned samples in an ultrahigh vacuum system using unmonochromatized Al $K\alpha_{1,2}$ radiation ($h\nu=1486.6$ eV, FWHM ≈ 1.2 eV).

Figure 1 shows the normalized XPS intensity of the Ge $3d_{5/2,3/2}$ core levels of some *a*-GeN alloy samples after Ar⁺ bombardment. The figure indicates that as more nitrogen is added into the *a*-Ge network, clear and significant shifts of *B*, the *3d* binding energy, and total line broadening due to new types of bonding appear. In the inset, we illustrate decomposition of the measured intensity in terms of Gaussian component line shapes, denoted by Ge1 and Ge2. The energies of these components in our samples relative to that in pure Ge (29.3 eV), or ΔB ,² are given in Table I. In analyzing the line shapes, a third, weak component appears, which we identify with an oxide component of germanium (e.g., GeO_x).³

The Auger Ge LMM transitions were also measured and analyzed in terms of the ¹*G* and ³*F* sets of doublets.^{2,4} As in the case of the XPS spectra, it was possible to decompose the

measured line shape in terms of two components, also identified as Ge1 and Ge2. The component energies relative to that in pure Ge (1144.9 eV),² or ΔK , are presented in Table I.

The resulting values of ΔB and ΔK of the component line shapes, Ge1 and Ge2 in Table I do not scale with nitrogen content, even though, from Fig. 1, it is clear that the higher the N content of the sample, the greater the intensity of the higher binding energy Ge *3d* components. Because of this shift invariance, we associate each of these components with a new chemical state. Since the Ge1 and Ge2 lines are 1.5 eV apart and 1.6 eV wide, we expect, from the SiN_x

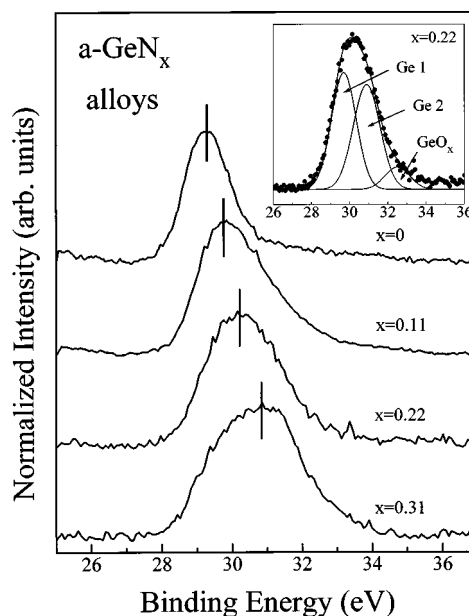


FIG. 1. Normalized XPS data for four different *a*-GeN samples. The observed features correspond to Ge $3d_{5/2,3/2}$ core levels and N-induced shifts. Observe the shift in the center of gravity of the core level and also the total line broadening as more nitrogen atoms are added to the *a*-Ge network. The inset shows the contribution of new Ge bonding configurations (due to the presence of N) through a Gaussian components deconvolution.

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TABLE I. Values of the energy of the component lines Ge1 and Ge2 of the measured spectra for the samples presented in Fig. 1 relative to the corresponding energies in pure Ge [29.3 eV and 1144.9 eV, respectively, for the pure Ge 3*d* and LMM (¹G₄)]. These shifts are the same for all the samples presented in Fig. 1. The Auger parameter shift is defined as $\Delta\alpha' \equiv -\Delta K - \Delta B$. The quantity Δn_{Ge} represents the change in valence charge of the Ge atoms calculated from the expression $\Delta\alpha' \equiv -\delta U \Delta n_{\text{Ge}}$, where $\delta U \equiv 1.5$ eV for Ge.

Ge 3 <i>d</i> shifts (eV)		Ge LMM shifts (eV)		$\Delta\alpha'$ (eV)		Δn_{Ge} (e ^l /atom)	
Ge1	Ge2	Ge1	Ge2	Ge1	Ge2	Ge1	Ge2
0.4	1.7	-1.0	-3.3	0.6	1.6	-0.4	-1.1

model,⁵ for Ge1 to incorporate the contributions of Ge atoms having, in our case, zero and one nitrogen bond and for Ge2 to correspond to a higher number of Ge—N bonds. The data for ΔB and ΔK in Table I allow us to determine, for each sample, the shift of the modified Auger parameter ($\Delta\alpha'$), where $\alpha' \equiv -(B+K)$,⁶ a quantity which is convenient for interpretation of the shifts, as is shown below.

One of the principal challenges in extracting electronic structure from electron spectroscopies is that of deriving atomic electron occupation changes from spectroscopic shifts. In order to appreciate the difficulties of interpretation, we display the expressions for the shifts in terms of fundamental quantities. The most commonly measured quantity is the XPS shift, which can be written⁷ as in Eq. (1), where we use atomic units ($|e| = \hbar = m = 1$)

$$\Delta B = - \int_0^1 dn_i \int d^3r \Delta\rho(n_i, n_j = 1; \mathbf{r}) r^{-1} + \Delta\mu, \quad (1)$$

where the spatial integral extends over all space and all energies are referred to vacuum. The quantity μ is the chemical potential and ρ denotes the self-consistent valence electron density of the solid, which is a function of the core electron occupations (n_i) of the photoionized atom (Ge here). The integral over n_i represents the transition from the system ground state to the core ionized final state of XPS.⁸⁻¹² The Auger kinetic energy shift for a transition involving only core levels ΔK is given by a similar expression.⁷

The difficulties in interpreting ΔB and ΔK arise from the difference in surface and chemical environment incorporated in $\Delta\rho$ and the difference in energy reference represented by $\Delta\mu$ when a range of compounds containing the photoionized species are compared. Analysis of $\Delta\alpha'$ is much simpler than that of the XPS and XAES shifts. From its definition we can express $\Delta\alpha'$ as in Eq. (2).⁸⁻¹¹

$$\Delta\alpha' = -\Delta \left(\int_0^1 dn_i \int d^3r [\rho(n_i, n_j = 0; \mathbf{r}) - \rho(n_i, n_j = 1; \mathbf{r})] r^{-1} \right). \quad (2)$$

In Eq. (2), there are two subtractions: the usual one between the sample of interest and the reference (Ge, in our case) and represented by the symbol Δ ; the other one is between the electron densities in the same sample corresponding to an initially ionized Ge and to a neutral Ge. The uncertainties

because of differences in chemical environment mentioned above in our discussion of the XPS and XAES shifts do not pertain. The only contribution to $\Delta\alpha'$ comes from that region of the charge density which responds differently, in the alloy and in the reference sample, to the charge state of the photoionized atom. Changes in the ground state valence charge produced by alloying on neighbors of the photoionized atom cancel.

The simplest approximation is to suppose that the core hole behaves like an extra proton (the equivalent core model). It is also convenient to separately consider contributions to $\Delta\alpha'$ from the region of the photoionized atom, whose atomic number is Z , and from its neighborhood. The contribution, $\Delta\alpha'_C$, from the region of the photoion becomes^{7,13-15}

$$\begin{aligned} \Delta\alpha'_C &= - \int_0^1 dn_i [U_v(Z+2-n_i) - U_v(Z+1-n_i)] \Delta n_v(Z) \\ &= - \delta U_v \Delta n_v, \end{aligned} \quad (3)$$

where U_v is the Coulomb integral of the photoion valence electrons, an atomic quantity which varies approximately linearly with Z , $n_v(Z)$ is its ground state valence occupation, and $\delta U_v \equiv \partial U_v / \partial Z$, a positive quantity (for Ge, $\delta U_v \equiv 1.5$ eV^{14,16}). If the type of screening is the same in both the sample of interest and the reference, then the only term in $\Delta\alpha'_C$ which survives is proportional to $\Delta n_v(Z)$. In our case, both the alloy and the pure Ge behave like insulators, so that we assume the type of screening to be unchanged in measuring the shift.

The contribution to $\Delta\alpha'$ from the neighborhood of the photoion comes from changes in the wave functions and changes in quantity of valence charge. Modification of the charge density by the positive core hole charge depends on the interatomic distance R as R^{-4} , so that this modification

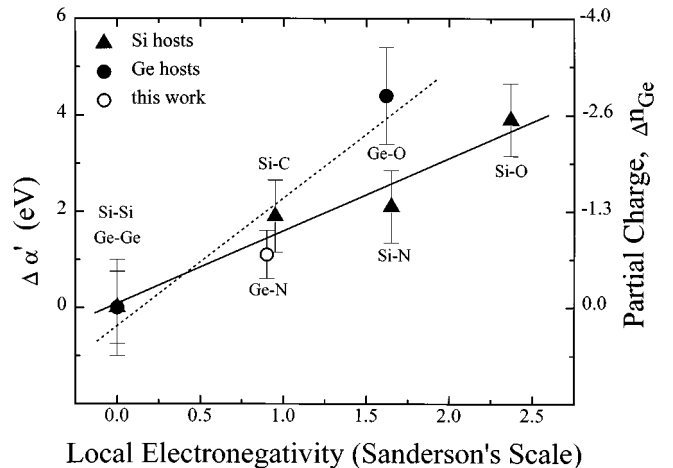


FIG. 2. Shifts of the modified Auger parameter induced in Si and Ge core levels as a function of the local electronegativity of the bonded impurity. The Ge—N data error bars correspond to values given by samples having different nitrogen content. Other error bars correspond to data dispersion from the literature (Ref. 3). A general trend is evident in the figure, the greater the local electronegativity the greater the corresponding chemical shifts. The right vertical axis indicates the partial charge to Ge derived from Eq. (3) for the nonstoichiometric compounds in the solid phase. The lines in the figure are linear regression fits of experimental data.

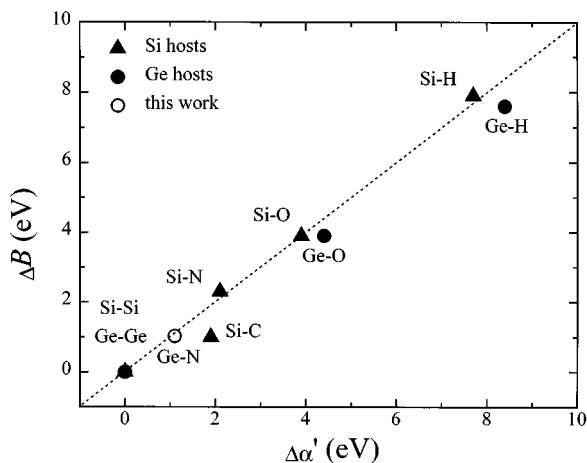


FIG. 3. XPS shifts of Si and Ge core levels as a function of the corresponding modified Auger parameter ($\Delta\alpha'$). The possibility of calibrating XPS shifts in terms of a scale based on the modified Auger parameter is clear.

should have little effect. There remains the possibility of incomplete screening of the photoion by its neighbors. In this case, each neighborhood atom would lose the valence charge, which might be important. This contribution is unknown, however, partially because of the nonstoichiometric character of the alloys and partially because of difficulties in calculating such charge changes accurately. Since the considered materials have insulator characteristics, we assume that there is no such loss of valence charge, and ignore this contribution. In the following, we examine the consequences of this assumption to see whether they agree with other, independent, considerations. It should be noted that the results of electronic transport measurements on the same *a*-GeN samples¹ and the widening of the pseudogap as the samples become nitrogen richer are in agreement with a diminishing ability of the host network (a decreasing number and/or mobility of electrons) to shield the created core holes.¹⁵

Application of $\Delta\alpha' \cong -\delta U \Delta n_{\text{Ge}}$ (where we drop the “valence” subscript) to the results in Table I yield $\Delta n_{\text{Ge}} \cong -0.4$ electrons for Ge1 and $\Delta n_{\text{Ge}} \cong -1.1$ electrons for Ge2, which should be compared with a loss of 1.5 electrons by the Ge atom in GeN_3 .¹⁷ If we interpret Ge1 as arising from one and Ge2 from two Ge—N bonds, then the analysis of $\Delta\alpha'$ would agree with a transference of approximately 0.5 electrons per Ge—N bond.

That Eq. (3) predicts proportionality between $\Delta\alpha'$ and Δn_{Ge} is reminiscent of the idea of the local electronegativity concept.¹⁷ Among the various electronegativity definitions and scales being reported in the literature, the one idealized by Sanderson,¹⁷ which was successful in explaining the IR transmission spectra of *a*-Si alloys,¹⁸ has been adopted here. Sanderson’s scale of electronegativity takes into account, besides the atoms “ability” to hold their own electrons tightly together, its electronic configuration.

For stoichiometric molecules in the gas phase containing either Si or Ge, it is possible to correlate XPS shifts and Si and Ge partial charges derived from the difference in electronegativity between the group IV element and the specific bonded impurity. The proportionality between $\Delta\alpha'$ and Δn_{Ge} from Eq. (3) raises the question whether there exists a

correlation between $\Delta\alpha'$ and the local electronegativity *even in nonstoichiometric materials*. The validity of such a correlation depends on a statistically significant number of samples. In Fig. 2, we present $\Delta\alpha'$ measured in a variety of samples containing either Si or Ge. The error bars associated with the data taken from the literature correspond to the dispersion of the reported values.³ Since the shifts correspond to quite different materials (different deposition methods and/or different impurity contents, for example), we take the point of view that the means of these shifts corresponds to some “average” environment. The value of $\Delta\alpha'$ corresponding to Ge—N, as determined in this work has been plotted in Fig. 2. As can be seen, the higher the local electronegativity, the larger the value of $\Delta\alpha'$.

The preceding considerations suggest the possible use of $\Delta\alpha'$ to define an electronegativity scale. In order to test this idea, we plot the XPS shift versus $\Delta\alpha'$ in Fig. 3 for the compounds in Fig. 2. The resulting linear correlation indicates first, the possibility of calibrating XPS shifts in terms of partial charges by use of Eq. (3) and second, that $\Delta\alpha'$ might furnish a reasonable scale of electronegativities in such nonstoichiometric solids.

Summarizing, in the present work we report the results of XPS and XAES measurements in substoichiometric *a*-GeN alloys, with nitrogen contents ranging from 0 to ≈ 30 at. %. We show under what circumstances measurement of $\Delta\alpha'$ permits the determination of the partial charge transfer to Si and Ge induced by different impurities in solid environments. The possibility of using $\Delta\alpha'$ as an electronegativity scale in solid Si and Ge compounds and as a calibration of XPS shifts is discussed and the limitations on such usage are outlined.

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