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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comments on "Electronic structure of hydrogenated and unhydrogenated amorphous SiN_x $(0 \leq x \leq 1.6)$: A photoemission study"

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Two major areas of disagreement exist. First, we believe that the D_{3h} symmetry about the nitrogen atom precludes the existence of a $2p_z$ lone-pair orbital there. Second, we believe that proper deconvolution of the Si $2p$ x-ray photoemission spectrum requires the use of doublets of fixed area ratio and fixed energy separation.

In a recent paper,[1] Kärcher, Ley, and Johnson carried out a large and detailed photoelectron study on amorphous silicon nitrides, covering both core and valence levels. These data were then used to interpret the chemical structure and bonding in such materials. Our own interest stems from the fact that we, too, are carrying out such studies.

While we can only admire the scope and extent of the experimental work, we must take issue with the way in which these data have been interpreted. Two major areas of disagreement exist: the authors' claim of the existence of lone-pair electrons on the nitrogen atom and the incomplete deconvolution of the Si $2p$ spectra.

THE EXISTENCE OF LONE-PAIR ELECTRONS ON THE NITROGEN

As Kärcher *et al.* point out, c-Si_3N_4 does indeed have D_{3h} symmetry about the nitrogen atom. However, contrary to their argument, this does not indicate that the highest occupied states are thus N $2p_z$ lone-pair orbitals. To understand this, one must note that the pyramidal structure of ammonia, with the hydrogen atoms lying in a plane below the nitrogen atom, is due to electron repulsion between the electrons in the N—H bonds and the $2p_z$ lone pair lying above the nitrogen atom and perpendicular to the plane of the hydrogen atoms.[2] On the contrary, the low-molecular-weight analogue of Si_3N_4, trisylyl amine, is planar about the nitrogen atom;[3] this D_{3h} symmetry is due to the fact that the lone pair is not localized on the nitrogen atom. Rather, these electrons have been delocalized into the silicon atoms through Si $3d\pi \leftarrow$N $2p\pi$ bond formation.[3,4] That is, the planarity about the nitrogen atom is due to the fact that there are no lone-pair electrons localized there to repel the other bonds or to function as a Lewis base.[5] This is so for Si_3N_4 as well. Thus, the interpretation of Kärcher *et al.*, that the band at the valence-band maximum seen in the ultraviolet photoemission (UPS) spectrum is due to the N $2p$ lone pair, is in error, as are the prior data upon which this conclusion is based (Refs. 21 and 51 of Kärcher *et al.*[1]).

THE DECONVOLUTION OF THE SILICON 2p SPECTRA

As with any such p-orbital spectrum, that for Si $2p$ is made up of two components, $2p_{3/2}$ and $2P_{1/2}$ in order of increasing binding energy, whose populations are in the ratio of 3:2 and whose peak-to-peak separations are 0.63 eV.[6] Thus, peak deconvolution must occur through the use of doublets of fixed area ratio and fixed separation. This was not done by Kärcher *et al.*, although they did allow for some asymmetry in the line shape and assumed that the linewidths for all silicon species would be as narrow as that for elemental silicon. This assumption has not been found to be true for most oxides.

We can suggest an alternative deconvolution and explanation of the x-ray photoemission spectroscopy (XPS) data, based on our own results. These were obtained on samples deposited in an SiH_4-NH_3 plasma and subsequently exposed to atmosphere. As seen in Fig. 1, the envelope is almost identical to that found for "$SiN_{1.5}$" by Kärcher *et al.*, in spite of the fact that they took precautions to prepare, transfer, and measure their samples under ultrahigh-vacuum conditions. Their spectrum also exhibited a minor peak near 99 eV binding energy, which we attribute either to elemental silicon or silicon hydride.[7]

Successful deconvolutions of our Si $2p$ envelopes were invariably accomplished using only two doublets each,

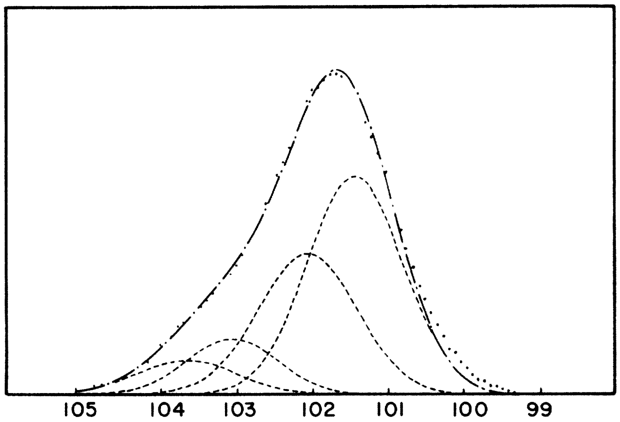

FIG. 1. A typical deconvoluted Si $2p$ envelope of a sample of a-SiN$_x$:H plasma deposited from a SiH$_4$-NH$_3$ mixture.

with full widths at half maximum of 1.4 and 1.5 eV, respectively. Under our conditions of manufacture, one doublet had a $2p_{3/2}$ peak maximum at 101.5 ± 0.2 eV and the other at 102.8 ± 0.2 eV. These values were insensitive, within the error quoted, to substantial variations in reactant ratios. For reference purposes, the $2p_{3/2}$ line position for crystalline elemental silicon was 99.3 eV.

Using recent XPS data measured on pure silicon compounds,[8,9] one may assign our peak near 103 eV to SiO$_2$ or to silicon oxynitride[7] which our variable takeoff angle data indicate is located near the surface. This is consistent with our previous findings for atmospheric exposure.[10] The peak near 101.5 eV may be identified with either Si$_3$N$_4$ (Ref. 11) or a lower oxide of silicon with 2 Si—O bonds.[12]

While the binding energies for SiO$_2$ given in the literature are slightly higher than that given here, the difference is accounted for by our measurement of a single component rather than the averaged position of the Si $2p$ doublet, as well as differences in energy referencing.[9] If SiO$_2$ were the only surface species present, it would account for a major fraction of the total measured oxygen, with the remaining oxygen bonded to a portion of the silicon observed at 101.5 eV. The remaining silicon is assumed to be bound to nitrogen and the Si-N ratio is calculated to be 1.0 ± 0.1. If the surface layer were totally oxynitride, the Si-N ratio would be 0.8 ± 0.1.

The invariability of the peak positions suggests that, at least under our conditions, only a limited number of major species are identifiable at the outer surface of deposited a-SiN$_x$:H. In this context, one final thing should be noted concerning the prior structural data[13,14] used by Kärcher *et al.* which indicated local order identical to that in c-Si$_3$N$_4$: those samples had their surfaces removed by diamond grinding prior to use. Thus, while bulk a-SiN$_x$:H may indeed resemble c-Si$_3$N$_4$, the surface, which is the region sampled by the XPS and UPS techniques used by Kärcher *et al.*, is substantially different.

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[1] R. Kärcher, L. Ley, and R. L. Johnson, Phys. Rev. B **30**, 1896 (1984).

[2] J. E. Huheey, *Inorganic Chemistry*, 2nd ed. (Harper and Row, New York, 1978), p. 201.

[3] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed. (Wiley-Interscience, New York, 1980), p. 378, and references therein.

[4] K. Kwart and K. King, *d Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur* (Springer-Verlag, New York, 1977), p. 16, and references therein.

[5] E. G. Rochow, *The Chemistry of Silicon* (Pergamon, New York, 1977), p. 1375.

[6] J. A. Bearden and A. F. Burr, Report No. NYO 10586, 1964, available from National Technical Information Service, Springfield, VA 22151.

[7] F. J. Grunthaner, B. F. Lewis, J. Maserjian, and A. Madhukar, J. Vac. Sci. Technol. **20**, 747 (1982).

[8] P. Streubel, R. Fellenberg, and A. Reif, J. Electron. Spectrosc. Relat. Phenom. **34**, 261 (1984).

[9] C. P. Wagner, in *Handbook of Photoelectron Spectroscopy*, edited by D. Briggs and M. P. Seah (Wiley, New York, 1984), p. 477.

[10] E. Sacher, J. Klemberg-Sapieha, M. R. Wertheimer, H. P. Schreiber, and R. Groleau, Philos. Mag. B **49**, L47 (1984).

[11] J. A. Taylor, Appl. Surf. Sci. **7**, 168 (1981).

[12] G. Hollinger and F. J. Himpsel, J. Vac. Sci. Technol. A **1**, 640 (1983).

[13] T. Aiyama, T. Fukunaga, K. Niihara, T. Hirai, and K. Suzuki, J. Non-Cryst. Solids 33, 131 (1979).

[14] M. Misawa, T. Fukinaga, K. Niihara, T. Hirai, and K. Suzuki, J. Non-Cryst. Solids **34**, 313 (1979).