



Use of carbon black to eliminate surface charging effects in photoelectron spectroscopy measurements of powders

M. N. Obrovac, Yuan Gao, M. N. Richard, and J. R. Dahn

Citation: [Applied Physics Letters](#) **71**, 2262 (1997); doi: 10.1063/1.120045

View online: <http://dx.doi.org/10.1063/1.120045>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/71/16?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Determination of graphene work function and graphene-insulator-semiconductor band alignment by internal photoemission spectroscopy](#)

Appl. Phys. Lett. **101**, 022105 (2012); 10.1063/1.4734955

[Analysis of charging effects on highly resistive materials under electron irradiation by using transient-absorbed-current method](#)

J. Vac. Sci. Technol. B **29**, 031209 (2011); 10.1116/1.3592188

[Accurate measurement of extremely low surface recombination velocities on charged, oxidized silicon surfaces using a simple metal-oxide-semiconductor structure](#)

Appl. Phys. Lett. **90**, 042104 (2007); 10.1063/1.2434172

[Precise determination of band offsets and chemical states in SiN/Si studied by photoemission spectroscopy and x-ray absorption spectroscopy](#)

Appl. Phys. Lett. **87**, 102901 (2005); 10.1063/1.2035894

[Studies of electrical and chemical properties of SiO₂/Si after rapid thermal nitridation using surface charge spectroscopy and x-ray photoelectron spectroscopy](#)

J. Vac. Sci. Technol. A **15**, 2787 (1997); 10.1116/1.580824

The image shows the cover of an Applied Physics Reviews journal issue. It features a blue and orange color scheme with a molecular structure background. The text 'NEW Special Topic Sections' is prominently displayed in white. Below it, 'NOW ONLINE' is written in yellow, followed by the title 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Use of carbon black to eliminate surface charging effects in photoelectron spectroscopy measurements of powders

M. N. Obrovac, Yuan Gao,^{a)} M. N. Richard, and J. R. Dahn^{b)}
Department of Physics, Dalhousie University, Halifax, Nova Scotia, B3H 3J5, Canada

(Received 16 June 1997; accepted for publication 14 August 1997)

The photoelectron spectra of SiO₂ on silicon powder is measured with and without the addition of carbon black. Samples without carbon black show significant charging and peak deformation due to photoelectron emission. Samples containing carbon black show no evidence of charging. Furthermore, the contribution from carbon black can be subtracted from the overall signal in the valence band region to give valence band spectra of insulating powders. It is suggested that mixing carbon black with nonconducting powders may be an effective way to eliminate surface charging effects while at the same time providing a useful calibration standard. © 1997 American Institute of Physics. [S0003-6951(97)00742-0]

Photoelectron spectroscopy (PES) is a powerful technique to study the electronic properties of materials. Ideally, samples for PES analysis are flat, conducting single crystals. However, many industrially relevant materials exist as nonconducting polycrystalline powders. It is well known that photoemission from nonconducting materials causes a positive surface charge which can shift electron energy distribution peaks to higher binding energies by many electron volts. Furthermore, irregular surfaces may charge nonuniformly, causing considerable peak deformation.¹ Many techniques have been developed to deal with surface charging and are reviewed in Ref. 2. These techniques can be categorized into two basic approaches.

The first approach is the use of reference peaks to calibrate the sample spectrum. Many reference lines have been suggested for this purpose. One of the most widely used references is the C 1s line because carbon is often present in samples as an impurity. Graphitic carbon has also been mixed directly with samples as a source of carbon because of its chemical inertness to many materials.²⁻⁴ Unfortunately, these calibration methods do not address the problem of nonuniform charging.

The second approach is to eliminate the surface charge completely. This may be accomplished by simply using thin film samples, if the material allows it. However, even then it is questionable whether the thin film accurately represents the bulk material. Low energy electron bombardment by means of a flood gun may also be effectively used to neutralize the surface charge. However, nonuniform charging can still occur with samples having an irregular surface morphology.¹

The removal of charge from insulating electrode powders has also been a problem in the battery industry.⁵ This has been remedied by the use of electrically conducting additives, the most common being carbon blacks. Carbon blacks differ from graphite in that small (10 nm) particles are linked to form long chains.⁶ When ground together with powders, the carbon black intimately connects the powder

particles in an electrically conducting network.

As previously mentioned, carbon in its graphitic form has been mixed with samples as a means of calibration. It has been suggested that "in addition to serving as a calibration standard, the graphite also ought to reduce surface-charge buildup on poorly conducting samples."³ In this letter, we suggest mixing carbon black with poorly conducting powder samples as a convenient way to eliminate the surface charge completely.

Photoelectron spectroscopy studies were carried out at the Canadian Grasshopper beamline located at the Synchrotron Radiation Center of the University of Wisconsin at Madison. The synchrotron beam was monochromatized by a Mark IV Grasshopper grazing incidence monochromator, with an energy range of 50–800 eV. The dispersion of the monochromator with the smallest slit setting is 0.03 Å. The photoelectrons were detected with a Leybold 180° hemispherical electron energy analyzer. It has a resolution of 0.8 eV with 100 eV pass energy. Details of the beamline can be found elsewhere.⁷

Silicon, obtained from Fisher as large chunks, was ground in air into a fine powder before use. Anhydrous LiOH (Johnson and Matthey, 99.95%) was used as obtained. Samples were prepared by thoroughly mixing an approximately 50/50 volume mixture of the sample powder and Super S Carbon Black (Chemicals, Inc.). This worked out to approximately 8% carbon black by weight for both the Si and the LiOH samples. The powder samples were then mounted with copper electrical tape onto a stainless steel block, which was grounded throughout the measurement. Measurements were carried out under ultra high vacuum conditions with the measurement chamber typically at $2-4 \times 10^{-9}$ Torr. Sample charging was detected by observing peak shifts when the incident photon flux was changed.

Figure 1(a) shows the Si 2p spectra of silicon powder samples with and without carbon black which we will call samples A and B, respectively. The dashed lines in the figure show the results of measurements taken with higher incident photon flux. Sample A shows two peaks at about 99 and 103 eV due to the silicon substrate and an SiO₂ surface layer, respectively. Only one broad peak shifted by about 10 eV due to charging can be seen in the Si 2p spectra of sample B.

^{a)}FMC Corp., Lithium Division, Bessemer City, North Carolina 28016.

^{b)}Departments of Physics and Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 3J5, Canada.

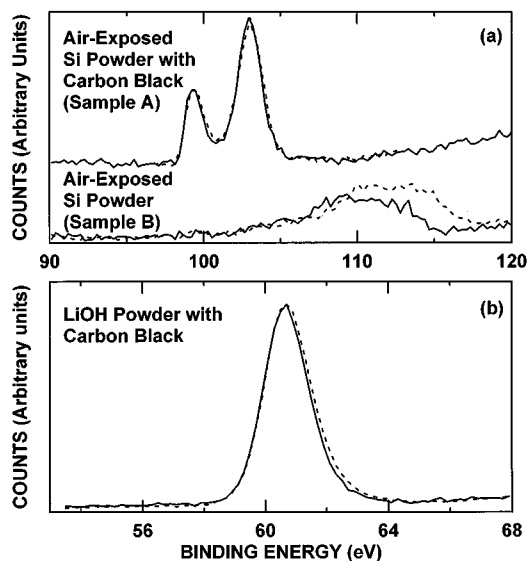


FIG. 1. (a) Si 2p spectra of silicon powders prepared with carbon black (sample A) and without carbon black (sample B). ($h\nu=170$ eV) (b) Li 1s spectrum of LiOH powder mixed with carbon black. ($h\nu=130$ eV) measurements taken at increased incident photon flux are shown with a dotted line.

The spectrum of sample B taken at a higher incident photon flux is markedly shifted to higher binding energy, thus indicating sample charging. Very little sample charging is apparent in the sample prepared with carbon black.

We have also done some preliminary PES measurements on ionic alkali powders. Figure 2(b) shows the Li 1s spectrum of LiOH powder mixed with carbon black. Very little evidence of charging was found in the sample.

Figure 2(a) shows the valence band spectrum of sample A. The valence band spectrum of pure carbon black is shown

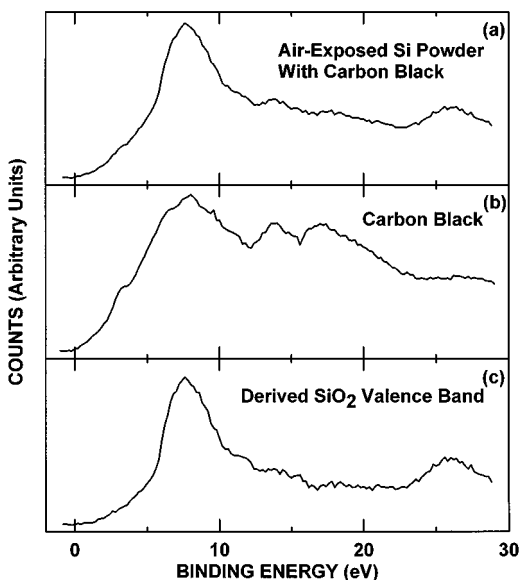


FIG. 2. Valence band PES spectra at $h\nu=130$ eV of (a) silicon powder mixed with carbon black (sample A) and (b) pure carbon black. Figure 2(c) was obtained by subtracting the appropriate amount of the carbon black valence band spectrum from the spectrum of sample A, so that the carbon black peaks are no longer visible. The binding energy is measured from the top of the carbon black valence band.

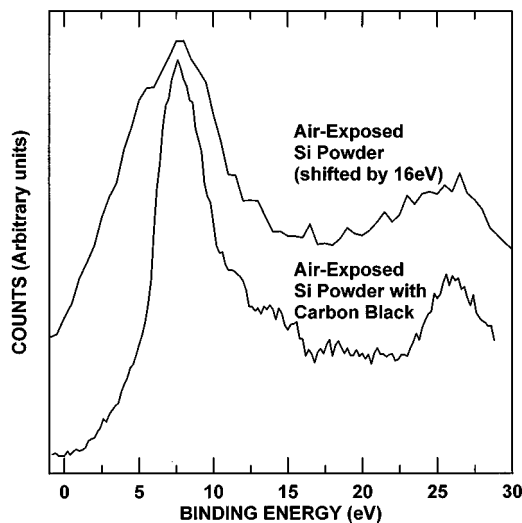


FIG. 3. Valence band PES spectra at $h\nu=130$ eV of silicon powder prepared with carbon black (sample A) and without carbon black (sample B). Binding energies are measured from the top of the carbon black valence band. The valence band of carbon black has been subtracted from the spectrum of sample A. The spectrum of sample B has been shifted by 16 eV to compensate for sample charging.

in Fig. 2(b). There is good agreement between the carbon black spectrum and previous XPS measurements of graphite,⁸ if one takes cross sections into account.⁹ Figure 2(c) was obtained by subtracting the appropriate amount of the carbon black valence band spectrum from the spectrum of sample A, so that the carbon black peaks at 3.3, 13.8, and 17.0 eV are no longer visible. We believe Fig. 2(c) is a good representation of the SiO₂ valence band spectrum, and it agrees well with earlier valence band measurements of more carefully prepared SiO₂ samples.^{10,11}

Figure 3 compares the valence band spectrum of sample A, with the carbon black peaks subtracted out, with the spectrum of sample B. The spectrum of sample B was shifted by 16 eV to compensate sample charging. No charging could be detected in sample A. Compared to sample B, the spectrum of sample A is much sharper and more features are visible.

In conclusion we have shown that effects of sample charging in photoemission measurements of powder samples can be significantly reduced by the addition of carbon black, enabling more detailed studies. This technique is especially useful for measuring core levels where there are no overlapping carbon features. The technique may also be applied to valence band measurements. However, in this region there are intervening features from carbon black. Thus measurements, under identical conditions, of carbon black standards must be made in order to subtract the carbon black features from those of the sample. Besides silicon, we have also done photoelectron studies on powder samples of transition metal oxide insulators mixed with carbon black that show no evidence of charging. It should be noted that, in addition to removing the surface charge, the C 1s line of carbon black may also be a useful calibration standard.

¹T. L. Barr, in *Practical Surface Analysis*, edited by D. Briggs and M. P. Seah (Wiley, Chichester, 1983), p. 283.

²A. Cros, *J. Electron Spectrosc. Relat. Phenom.* **59**, 1 (1992).

- ³R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.* **9**, 2469 (1970).
- ⁴G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.* **2**, 295 (1992).
- ⁵D. W. McComsey and W. B. Felegyhazi, *Handbook of Batteries*, edited by D. Linden (McGraw-Hill, New York, 1995), p. 8.12.
- ⁶See, for example, Shawinigan Acetylene Black data sheet, available from: Chevron Chemical Company, Olefins & Derivatives Division, P.O. Box 3766, Houston, TX 77235.
- ⁷K. H. Tan, G. M. Bancroft, L. L. Coatsworth, and B. W. Yates, *Can. J. Phys.* **60**, 131 (1982).
- ⁸F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Cavell, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B* **9**, 5268 (1974).
- ⁹J. J. Yeh and I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).
- ¹⁰B. Fischer, R. A. Pollak, T. H. DiStefano, and W. D. Grobman, *Phys. Rev. B* **15**, 3193 (1977).
- ¹¹S. T. Pantelides and W. A. Harrison, *Phys. Rev. B* **13**, 2667 (1976).