

Analysis of Fe nanoparticles using XPS measurements under d.c. or pulsed-voltage bias[†]

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The impact of solution exposure on the charging properties of oxide coatings on Fe metal-core oxide-shell nanoparticles has been examined by sample biasing during XPS measurements. The Fe nanoparticles were suspended in relatively unreactive acetone and analyzed after particles containing solutions were deposited on SiO₂/Si or Au substrates. The particle and substrate combinations were subjected to ± 10 V d.c. or ± 5 V a.c., biasing in the form of square wave (SQW) pulses. The samples experienced variable degrees of charging for which low-energy electrons at ~ 1 eV, 20 μ A and low-energy Ar⁺ ions were used to minimize it. Application of d.c. bias and/or SQW pulses significantly influences the extent of charging, which is utilized to gather additional analytical information about the sample under investigation. This approach allows separation of otherwise overlapping peaks. Accordingly, the O1s peaks of the silicon oxide substrate, the iron oxide nanoparticles, and that of the casting solvent can be separated from each other. Similarly, the C1s peak belonging to the solvent can be separated from that of the adventitious carbon. The charging shifts of the iron nanoparticles are strongly influenced by the solvent to which the particles were exposed. Hence, acetone exhibited the largest shift, water the smallest, and methanol in between. Dynamical measurements performed by application of the voltage stress in the form of SQW pulses provides information about the time constants of the processes involved, which leads us to postulate that these charging properties we probe in these systems stem mainly from ionic movement(s). Copyright © 2010 John Wiley & Sons, Ltd.

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Introduction

Use of granular zero-valent iron metal, Fe⁰, or bimetallic combinations with catalytic metals such as Pd, for removal of contaminants from soil and water, has recently gained significant attention, since the nanoparticles may be delivered to deep contamination zones by injection, and that nano-sized Fe⁰ may be more effective at degrading some contaminants.^[1,2] The appealing aspect of this technology has led to its rapid adoption by the community, and field demonstrations have already been carried out to reveal their greater rates for decontamination.^[3,4] Nano-sized Fe⁰ particles exhibit greater reaction rates primarily in proportion to their increased surface areas.

Owing to their high reactivity, in most environments nanoparticles containing Fe⁰ will be surrounded by some type of passivating layers such as a shell of oxides. Such passivating layers may be deliberately formed, or form with time, as particles are handled in different environments. We have previously found that the properties of the nanoparticles change as a function of time due to exposure to water,^[5] and have the evidence suggesting that contaminants such as S will alter the reactivity of the particles. Preparation, characterization and properties of these iron metallic nanoparticles have been recently reported by us using a number of spectroscopic, including XPS, and electrochemical methods.^[5,6] There are several challenges to understanding the properties of these nanoparticles as they change in solution. First, it is necessary to extract them from the solution if an *ex situ* analysis is to be performed. On the basis of earlier studies, this has been accomplished by a 'flash-drying' process conducted in a glovebox using a solvent to wash out water, and a moderate vacuum to remove solvents.^[5] Second,

because of the time dependence of the reactivity of the nanoparticles in solution we are particularly interested in understanding the characteristics of the oxide shell as a function of time in solution. Because the initial shell appears to be relatively unreactive^[6] we are interested in determining if sample biasing can be used to examine the conducting properties of the oxide shells, and ultimately, if it can be used to examine changes in those properties.

In the present contribution, we focus on examining the properties of nano-Fe⁰ particles that have been exposed to acetone and deposited on an oxidized Si wafer using a modified version of the XPS, where charging properties of these particles are enhanced and probed in a controlled fashion. Our method is based on controlling the electron flood current through application of external voltage bias to the sample. For these initial tests of this method, the test selection of particles was suspended in acetone and placed on the substrate in a nitrogen environment and allowed to dry. Although not presented in detail, differences between the measurements using acetone are reported here, and those involving methanol and water are described.

During data acquisition in XPS, a finite, measurable, and more or less steady current (0.1–20 nA) flows through the sample due

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to the generated photo and secondary electrons, which usually causes unwanted positive charging in poorly conducting samples or parts of surface heterostructures.^[7–11] A great deal of effort has been devoted to compensate and overcome this charging, and very successful techniques have been developed, mostly using directed flow of low-energy electrons (and sometimes ions) from an external unit (flood-gun) to the sample. However, complete removal of charging is only an ideal, and excessive flooding can also cause negative charging.^[11–13] Such negative charging, sometimes identified as controlled surface charging (CSC), has also been utilized to extract information related with some chemical/physical properties of surface structures, even down to monolayers.^[14–17] During an XPS measurement, the total current flowing through a sample is the sum of electrons going out of that sample due to photoemission. And almost as importantly, the secondary electrons, as well as the electrons going into that sample due to electrons or ions from the flood gun(s), or stray electrons. Some components of the total current can easily be controlled by application of a small (0–10 V) external voltage in the form of d.c. bias and/or a.c. pulses, as has been reported recently.^[18–19] The effect of this applied voltage bias can then be assessed in the measured line positions. If the sample under investigation is a good conductor, the effect will manifest itself as trivial voltage shifts in the positions equivalent to the applied bias. For poorly conducting samples, however, this will emerge as nonlinear shifts due to operation of various charging/discharging processes. These shifts can be utilized to extract both static and dynamic information about charge transport processes, when, respectively, d.c. and a.c. bias are applied. Core-level XPS is especially attractive since additional chemical information can be derived for specific chemical components from the line positions of the corresponding peaks since the measured line positions are altered by local potentials developed due to the uncompensated charges.

Experimental

Details of the preparation of the nano-Fe⁰ nanoparticles are given in our earlier publications.^[5,6] Particles were deposited on Au, a Si wafer with the native oxide and a Si wafer which had been heat treated in an oven for 2 h at ~630 °C to increase the thickness of the surface oxide to ca. 8 nm. The solutions containing the particles were deposited on the substrate and left to evaporate inside the nitrogen-purged glovebox, and the sample mounting was performed inside the nitrogen-purged I²R glovebox attached to the XPS sample introduction chamber. This glovebox was continually purged with nitrogen (<1 ppm oxygen) from LN₂ evaporation. XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system uses a focused monochromatic Al K α X-rays (1486.7 eV) source and a spherical sector analyzer. The samples experienced variable degrees of charging for which low-energy electrons at ~1 eV, 20 μ A, and low-energy Ar⁺ ions were used to minimize it. Application of d.c. bias and/or SQW pulses drastically influences the extent of charging, which was utilized to gather additional analytical information about the sample under investigation.

Results and Discussion

The charging shifts for samples deposited on different substrates vary depending on the substrate. Since the largest variations in

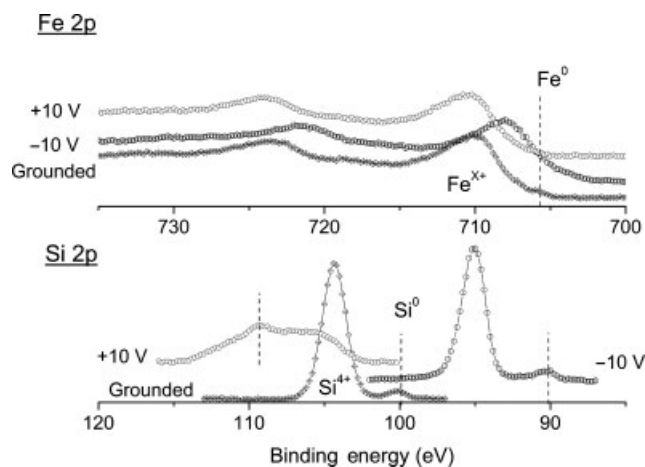


Figure 1. Si2p and Fe2p regions of the XPS spectrum of Fe-nanoparticles cast from acetone and deposited on a silicon substrate containing ca. 8 nm oxide layer, recorded when grounded, and under +10 and –10 V voltage stresses, respectively.

charging for different sample treatments were observed for the oxidized Si substrate, those results are reported here. The presence of a buffering dielectric layer appears significant in this work and is subject to additional study. Survey spectra of such deposited FeNP from acetone or other solutions on the oxidized Si substrate show both, Fe from the nanoparticles, and Si from the substrate. As one example, the atomic composition of the surface calculated assuming a uniform layer from one survey spectra of particles deposited from acetone was 60 at% O, 21 at% Si, 13 at% Fe and 5 at% C. In Fig. 1, we display the Fe2p and Si2p peaks recorded on the Fe nanoparticles deposited in acetone on the oxidized Si substrate when the sample was grounded, and subjected to –10 and +10 V external bias. The O1s and C1s photoelectron peaks display similar shifts. For conducting samples, application of a voltage bias would result in a trivial shift in the energy scale, hence, when corrected accordingly, the peak position coincides with that of the grounded spectrum. This is the case for the Si2p peak corresponding to that of the Si⁰ underlayer. However, for the SiO₂ dielectric layer and the Fe nanoparticles, the situation is quite different due to charging. Each layer or surface structure experiences a different extent of charging.

It is easiest to understand the SiO₂ shifts since this system has been widely investigated. The Si2p binding energy for a heavily n-doped Si is 99.7 eV, and the corresponding one for Si⁴⁺ is 103.4 eV when it is in a truly uncharged zero point charge (ZPC) state which increases when the layer is positively charged (hole-traps created), and decreases when negatively charged (electron traps created).^[7,12,13] In Fig. 2, we redisplay the Si2p region after correcting for the trivial bias shift, where we see that both, in the grounded case and under negative bias, the oxide layer is positively charged, which indicates that the flood-gun is not 100% effective. Application of the positive bias severely distorts the oxide Si2p peak due to strong inhomogeneous negative charging. Note, however, that the Fe2p peak (shown in Fig. 1), although shifted, is not distorted at all.

The charging shifts in the peaks, between the grounded and under the –10 V bias spectra are significant enough to carry out analysis. Hence, from now on, we will consider only these differences, which are given in Fig. 3. There are two important differential charging shifts observed corresponding to i) the 0.6 eV difference in the Si2p of the SiO₂ layer, and ii) the 8.1 eV difference

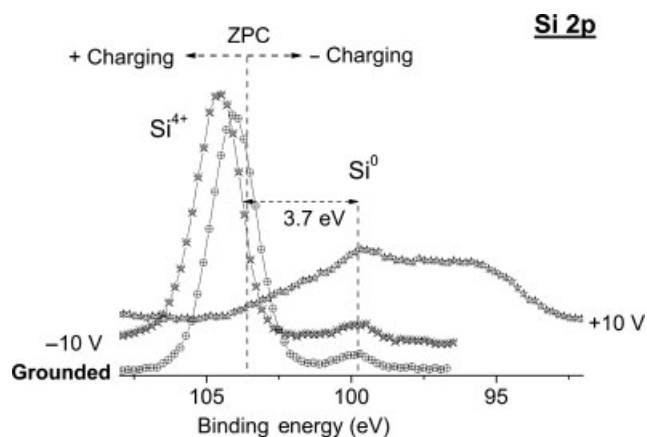


Figure 2. The Si2p region shown in Fig. 1, after correcting for the trivial voltage shifts.

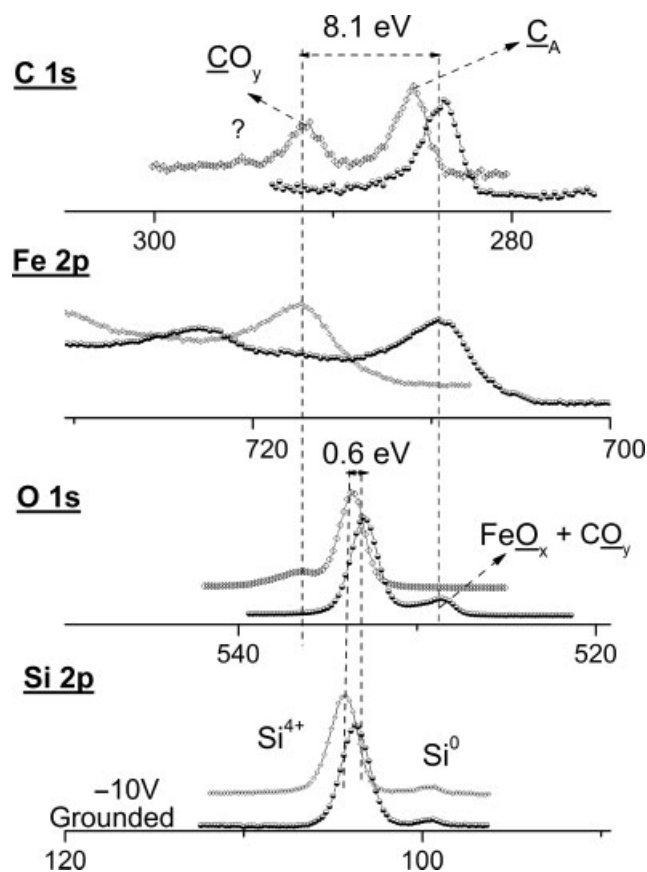


Figure 3. The grounded (\circ) and under -10 V voltage stresses (\diamond) Si2p, O1s, Fe2p and C1s regions of the same sample after employing the correction.

in the Fe2p of the iron-oxide nanoparticles. Under -10 V bias, the C1s peak splits into two components, one of which exhibits exactly the same shift as the Fe2p peak. The O1s has two components for both the grounded and -10 V bias spectra. These components show a 0.6 and 8.1 eV difference in between allowing them to be associated with the shifts observed for Si and Fe. The large O1s component which is at 533.0 eV in the grounded spectrum, and shifts to the extent of only 0.6 eV, belongs to the SiO₂ layer, and the small O1s component at 529.0 eV in the grounded

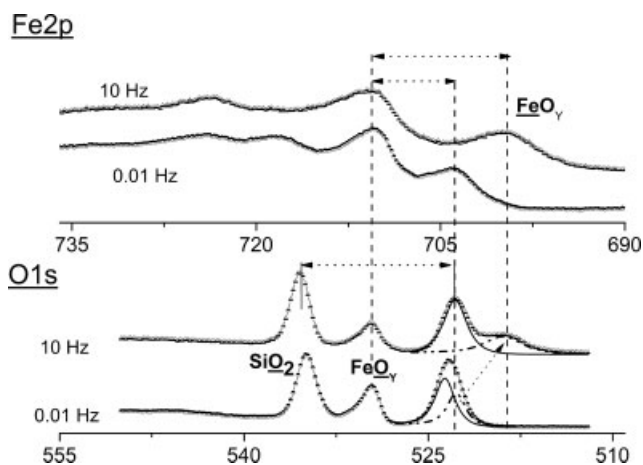


Figure 4. The Si2p and the Fe2p regions recorded while applying SQW pulses with 5 V amplitude at 10 and 0.01 Hz frequencies.

spectrum, which exhibits 8.1 eV shift, can now be assigned as resulting from the iron oxide, and possibly, residue from the casting solvent, acetone. Appearing as a single component in the grounded spectrum, the C1s decomposes into three components; belonging to adventitious carbon, designated as (C_A) in the figure, carbon associated with the nanoparticles (based on earlier work likely including the casting solvent^[6]) and, doubtfully, a small component, designated as (?) in the figure, possibly due to oxidized solvent or the presence of carbonates. The simplicity and the power of the method is overwhelming, since it not only gives us additional resolving power, but also paves the way to determining complete chemical composition of the nanoparticles, and also the casting solvent surrounding it, after correcting for the corresponding cross-sections.

Furthermore, it is interesting to observe that the casting solvent residue and the iron nanoparticles exhibit exactly the same very large 8.1 eV charging shift, which means that the thin surrounding solvent layer is in intimate electrical contact with the iron/iron oxide particle. When the same nanoparticles cast from methanol and water were investigated (not shown here), the corresponding shifts were measured as ca. 2.0 and 0.5 eV, respectively, indicating that the charging properties of these nanoparticles are dominated by the solvent (acting most probably as a double-layer capacitor) and any solvent-induced changes in properties of the nanoparticles themselves. The trend (water < methanol < acetone), is consistent with what would be expected for double-layer charging since the voltage developed would depend inversely on the dielectric constant of the layer.^[20]

Dynamic information about the charging processes can be extracted from data collected while applying the stress in the form of SQW pulses with different frequencies, as displayed in Fig. 4. The pulses complicate the appearance of the spectra because all the peaks appear in duplicate. However, for dielectric surface structures, the positions of the duplicated peaks are strongly frequency-dependent, which may be used for extracting information about the dynamics of the charging/discharging processes. The data shown in the figure corresponds to pulses with an amplitude of ± 5 V, hence, a peak representing a conducting feature would be duplicated at -5.0 and $+5.0$ eV, with an exact 10.0 eV separation. For nonconducting samples, less than 10.0 eV separation will be observed. Furthermore, at low frequencies the separation gets smaller since ample time is allowed for the system

to charge and discharge.^[19] Since both the SiO₂ layer and the Fe particles are not highly conductive, we observe less than 10.0 eV separation for both of them, but the shift is less for the Fe particle peaks. The d.c. bias experiments help with peak identification of the O components. At 0.01 Hz, both the O 1s peaks of SiO₂ and FeO_y appear as resolved peaks on the positive cycle of the pulse (the left-hand side), but they merge into each other on the negative cycle (the right-hand side). At 10.0 Hz they are resolved for both positive and negative bias, but the FeO_y peak is broadened at the lower BE (−5V bias) side. The corresponding Fe 2p peaks also follow the same trend. What emerges out of these measurements is that the charging/discharging dynamics are slow on the order of 0.1–10 s which indicates that they are definitely not related with fast electron transfer and/or dipole orientations, but are due to ionic processes. Since we are interested in understanding the ionic conductivity of the nanoparticles this is an interesting observation. Initial experiments for particles exposed to water indicate that the conductivity is significantly altered.

Detailed examination of these peaks is expected to shed light on the chemical origin of the charging process and the underlying physicochemical phenomena (double-layer charging, particle alteration, etc.) causing it. Correlation between electrochemical data (impedance), especially with regard to the effects of aging, would yield invaluable information.^[5]

Conclusions

The technique of applying d.c. voltage stress to the sample while measuring XPS data has enabled us to control the charging properties via which we were able to decompose, assign and eventually quantify the peaks representing the silicon oxide substrate, the iron nanoparticle and the casting solvent (acetone). The charging shifts of the iron nanoparticles are strongly influenced by the surrounding solvent. Dynamical measurements performed by application of the voltage stress in the form of SQW pulses led us to postulate that these charging properties stem mainly from ionic movement(s).

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