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Formation of nanostructured Group IIA metal activated sensors: The transformation of Group IIA metal compound sites

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ABSTRACT

Trends in the Group IIA metal oxides and hydroxides of magnesium, calcium, and barium are unique in the periodic table. In this study we find that they display novel trends as decorating nanostructures for extrinsic semiconductor interfaces. The Group IIA metal ions are strong Lewis acids. We form these M^{2+} ions in aqueous solution and bring these solutions in contact with a porous silicon interface to form interfaces for conductometric measurements. Observed responses are consistent with the formation of MgO whereas the heavier elements display behaviors which suggest the effect of their more basic nature. $Mg(OH)_2$, when formed, represents a weak base whereas the heavier metal hydroxides of Ca, Sr, and Ba are strong bases. However, the hydroxides tend to give up hydrogen and act as Brönsted acids. For the latter elements, the reversible interaction response of nanostructures deposited to the porous silicon (PS) interface is modified, as the formation of more basic sites appears to compete with M^{2+} Lewis acidity and hydroxide Brönsted acidity. Mg^{2+} forms an interface whose response to the analytes NH_3 and NO is consistent with MgO and well explained by the recently developing Inverse Hard/Soft Acid/Base model. The behavior of the Ca^{2+} and Ba^{2+} decorated interfaces as they interact with the hard base NH_3 follows a reversal of the model, indicating a decrease in acidic character as the observed conductometric response suggests the interaction with hydroxyl groups. A change from oxide-like to hydroxide-like constituents is supported by XPS studies. The changes in conductometric response is easily monitored in contrast to changes associated with the Group IIA oxides and hydroxides observed in XPS, EDAX, IR, and NMR measurements.

1. Introduction

The concept of chemical hardness/softness first developed by Pearson [1–4] is based on the nature of metal ion complexation in aqueous solution and is a generalization of the Lewis acid/base concept. Within this concept, hard acids combine with hard bases to form strong ionic bonds whereas soft acids combine with soft bases to form covalent bonds. This is the tenant of the HSAB concept. In contrast, the inverse hard/soft acid/base (IHSAB) concept [5], designed to model reversible sensor response, is based on weak interactions. These weak interactions result in the effective transfer of electron density in the absence of chemical bond formation to an appropriate interface. This requires that hard acids interact with soft bases and vice versa. The IHSAB and HSAB concepts are complementary and correlate with the same basic parameters associated with electronic structure theory [6–16]. The highest occupied molecular orbital (HOMO) of a donor analyte and the lowest unoccupied molecular orbital (LUMO) interact. The IHSAB principle, within the acid/base concept, focuses on a HOMO–LUMO mismatch to minimize chemisorption and induce the efficient transfer of electrons. The IHSAB concept as it models electron transfer from a variety of chosen nanostructured metal oxide-based deposits to an extrinsic porous silicon semiconductor signals a range of responses [17,18] that can be used to design and create sensitive sensor platforms [5,19–22]. We link chemical

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Abbreviations: XPS, X-ray photoelectron spectroscopy; NMR, nuclear magnetic resonance; EDAX, energy dispersive X-ray analysis; IR, infrared; IHSAB, inverse hard/soft acid/base; PS, porous silicon; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; UHP, ultra high purity; SEM, scanning electron microscopy; XRD, X-ray diffraction; MeOH, methanol; TBAP, tetrabutylammonium perchlorate; MeCN, acetonitrile; DFT, density functional theory; PES, photoemission spectroscopy; DI, deionized.

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selectivity and the mechanism of sensor response. The IHSAB principle enables the selection of analyte–interface interactions from materials that do not form strong covalent or ionic chemical bonds (see also Supporting material).

This study focuses on the oxides and hydroxides of the hard acids of the Group IIA metals. In strong contrast to the remaining elements of the periodic table, the Group IIA metals form hydroxides, which are decidedly of comparable or greater stability than the corresponding metal oxides. $Mg(OH)_2$ represents a weak base, whereas the heavier metal hydroxides of Ca, Sr, and Ba are known to form strong bases [23]. However, since the dihydroxides can donate a hydrogen they are classified as Brönsted acids. Based on the conductometric responses with respect to decorated *p*-type PS we report herein, the Mg^{2+} sites appear to act as oxide-based Lewis acids. This conductometric interaction is modified for the heavier Group IIA compounds indicating a virtual reversal in the interaction of a decorated PS interface to NH_3. This process causes a much more significant change than *in situ* nitridation [24,25]. Within this study an important observation is that the changes in conductometric reversible response and acid/base interaction are easily monitored for very small M^{2+} deposition concentrations. This is in sharp contrast to the corresponding changes associated with the transformation of the Group IIA oxides to their hydroxides as measured by X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDAX), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) measurements.

2. Experimental

2.1. Sensor fabrication

The experimental procedures used here have been discussed previously [5,17,26–28]. Nanopore covered micropores are formed with a hybrid etch procedure [5,29,30]. Evaluations have led to the conclusion [5] that a decorated microporous structure is optimal for gas phase sensor study. The nanoporous coating is fundamental to trapping nanostructured materials. The porous silicon (PS) interface depicted in Figs. S1 and S2 is generated from 1 to 20 Ω-cm, *p*-type (boron doped) (1 0 0) silicon wafers by first depositing an insulating layer of SiC by plasma-enhanced chemical vapor deposition (PECVD) and then using standard photolithography methods and reactive ion etching (RIE) to open up 2 mm by 4 mm windows of the SiC to expose the bulk Si. The *p*-type wafers are then etched in 1 M HF, and 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile (MeCN) at 3–6 mA/cm^2. The PS has a porosity of 50–80% with the micropore diameters varying from 0.8 to 1.5 μm and pore depths varying from 10 to 30 μm. Finally, a 3000 Å gold contact is deposited by e-beam evaporation.

2.2. Group IIA metal deposition

The selection of the nanostructures and the variable surface sensitivities that are produced as they form distinct nanostructured deposits provides design systematics. The nanostructures are deposited fractionally to the PS micropores in a process that does not require self-assembly or an exacting film arrangement. However, the nanostructure deposition concentration must be maintained at a sufficiently low level to avoid cross-talk between the nanostructures that can lead to an eventual loss of functionality. There is a “percolation” threshold above which sensing activity drops [22,27,31]. A small fraction of the micropores are covered with the metal oxide nanostructures [27,31]. The optimum concentration of the nanostructure directing deposits is dictated by the acidic or basic character of the deposited nanostructures and the nature of the electron density associated with each cluster [21,22,27]. The concentrations of the Group IIA metals Mg, Ca, and Ba optimum deposition concentrations are approximately an order of magnitude lower than the metal oxide sites we have previously studied [5,21,25,27]. This method of generating modified interfaces provides nanostructure decorated island sites producing interfaces that appear to be more sensitive than those previously obtained [3,4,6]. The nanopore coating of the micro-channel suppresses nanostructure agglomeration, both during deposition and when in use as a sensor.

Untreated PS hybrid structures, with an exposed PS area of 4 mm^2, are fully submerged in 0.02 M to 0.05 M Group IIA metal-based aqueous solutions, in which the metal dichlorides are fully dissolved. These preparations are expected to initially produce the hydrated Group IIA ions, M^{2+} and Cl^- and subsequently the metal oxides and hydroxides ($MgCl_2$, $K_{sp} = 738$; $CaCl_2$, $K_{sp} = 1210$; $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{-12}$; $Ca(OH)_2$, $K_{sp} = 5 \times 10^{-6}$; $Ba(OH)_2$, $K_{sp} = 5 \times 10^{-3}$) or combinations thereof. The solubility in water of the metal hydroxides increases with increasing atomic number but is notably lower than the chlorides. The PS interfaces are exposed to these solutions for 15 s. After the 15 s exposure they are subsequently placed in deionized (DI) H_2O for a 120 s period and rinsed in MeOH for 120 s. The nanostructure sites studied with X-ray diffraction (XRD) appear to correspond to amorphous structures, which display no diffraction pattern [29]. However, this might be attributed to the extremely small amount of deposited material. It is unlikely that crystallization occurred during the short deposition and subsequent surface cleaning process, as the deposition solutions were prepared from the metal dichloride dissolved in DI H_2O.

Sensing depends primarily on the electronic interaction of the nanoparticles, as each particle must operate independently of the other particles, and its electronic interaction with the surface/substrate. Scanning electron microscopy (SEM) data for several samples indicates a significant physical separation between the nanoparticles even at the highest concentrations used in this study [39]. However, at these concentrations there is strong evidence for cross-talk between the nanoparticles. While the HOMO–LUMO gap/mismatch inherent to the IHSAB concept must be size dependent, the distribution of particle sizes used in these studies, 10–30 nm [5,17,19,21–29,31], does little to vary this energy gap and its importance relative to the requirement of electronic separation (particle cross-talk). The requirement of electronic separation is overwhelmingly the dominant factor controlling the quality of sensing and the particles need not be mono-dispersed [39].

2.3. Gas detection

All sensors are evaluated in an unsaturated mode since the time scale for reversibility may become an issue in a long term saturated mode. These longer-term exposures are not necessary because each sensor before and after deposition is tested under identical conditions. NH_3 or NO was pulsed onto the decorated interfaces with a 120 s half-cycle followed by a 240 s nitrogen cleaning. The system was purged with ultra-high purity (UHP) nitrogen for 1800 s before operation. The sensor response and recovery times for “sticky” gases, such as ammonia, are distinctly different and full time recovery from the gas exposure takes longer than 120 s, the exposure time duration in the present configuration (Fig. 2 in [17]). However, the onset of the sensor response remains clearly visible. The response for NH_3 on PS is that of a gas whose interaction may be dominated by physisorption but which also displays weak chemisorption. Purging the sensor surface with UHP N_2 for longer durations improves the shift to the initial base line. Nitridation with NH_3 and NO is irrelevant in this experiment as it is a process that requires treatment for several hours at elevated