Adsorption of mercaptosilanes on nanocrystalline and single crystal zinc oxide surfaces

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ABSTRACT

The wide band gap and unique photoluminescence (PL) spectrum of nanocrystalline zinc oxide (nano-ZnO) make it attractive for a variety of photonics and sensor applications. Toward the goal of modifying the electronic structure and optical properties of nano-ZnO, the adsorption of 3-mercaptopropyltriethoxysilane (MPTES) has been investigated. Nano-ZnO rods having widths of 10-20 nm and lengths of 100-300 nm were functionalized by ultrasonicating them in a hot ethanol/water solution and adding MPTES. FTIR and X-ray photoelectron spectroscopy (XPS) of the modified nano-ZnO confirm silane functionalization. The presence of hydroxyl groups prior to functionalization suggests that adsorption to ZnO occurs primarily via a condensation reaction and the formation of Zn-O-Si bonds. Comparison has been made to 3-mercaptopropyltrimethoxysilane (MPTMS) adsorbed in ultrahigh vacuum onto sputter-cleaned single crystal ZnO(0001) in which MPTMS vapor is leaked into the vacuum chamber. In this case, bonding occurs via the thiol groups, as indicated by angle-resolved XPS studies. Similar experiments in which sputter-cleaned ZnO(0001) is dosed with dodecanethiol (DDT) confirm adsorption via S-Zn bond formation. Photoluminescence measurements of MPTES-functionalized nano-ZnO show an increase in intensity of the UV emission peak and a decrease in the visible peak relative to the unfunctionalized particles. The reduction of the visible emission peak is believed to be due to passivation of surface defects.

Keywords: metal oxide, nanocrystalline, photoelectron spectroscopy, photoluminescence, silanes, thiols, zinc oxide

1. INTRODUCTION

Zinc oxide is a wide band-gap semiconducting material that offers unique opportunities for biological and chemical sensor applications[1] because of its combination of UV and visible photoluminescence (PL) peaks. The UV and visible peaks originate from band-edge and defect emission, respectively.[2,3] Specifically, the (usually green) visible emission peak has been postulated to be due to a transition between an oxygen vacancy and a photoexcited hole.[4] Because oxygen vacancies are prominent on the surface, it is interesting from a sensor perspective to attempt to tailor the PL spectrum by adsorption of covalently bonded molecules to the ZnO surface.

It has been experimentally demonstrated[1,5,6] that organosilanes may adsorb on ZnO surfaces under acidic conditions via hydrolysis of alkoxysilane groups on a hydroxylated surface and formation of Zn-O-Si bonds. However, the process is complicated by the crystallinity of the surface, the presence of defects, the nature of the adsorbate and adsorption conditions, as illustrated by recent molecular dynamics simulations.[7] It has also been shown that alkanethiols may adsorb on ZnO surfaces. For example, Norton and colleagues[8] investigated the adsorption of dodecanethiol on ZnO by immersing zinc- and oxygen-terminated ZnO surfaces in the thiol solution, and it was shown by XPS that the S2p signal was present and persisted even after heating to 400°C. This provided strong evidence of covalent bond formation to the

Nanophotonic Materials V, edited by Zeno Gaburro, Stefano Cabrini, Dmitri Talapin
Proc. of SPIE Vol. 7030, 70300T, (2008) · 0277-786X/08/$18 · doi: 10.1117/12.794805

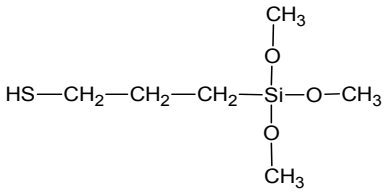
ZnO surface. Recent studies by Halevi and Vohs[9] demonstrated that methanethiol reacts preferentially at step edges and may adsorb dissociatively. Furthermore, it was shown that octanethiol can quench the growth of ZnO nanoparticles via adsorption onto facets of nanocrystalline ZnO.[10] Adsorption studies by Taratula *et al.*;[11] however, using FTIR attenuated reflectance spectroscopy, indicated that hexanethiol did not bind to nanotip ZnO films. Petoral *et al.*[12] studied the adsorption of 3-mercaptopropyltrimethoxysilane on several semiconductor surfaces, including epitaxial layers of ZnO grown on the c-plane of sapphire. These authors showed that the adsorbate could bond to the surface via both the silane and thiol groups, with 30-50% of the molecules attached via the silane group of the molecule and the remainder via the thiol group. It was hypothesized that the molecule adsorbed via its silane end to hydroxylated sites and via its thiol end to zinc sites.

In the present study we report the functionalization and characterization of nanocrystalline ZnO with 3-mercaptopropyltriethoxysilane (MPTES) using photoluminescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. Comparison has been made to experiments in which 3-mercaptopropyltrimethoxysilane (MPTMS) and dodecanethiol (DDT) have been adsorbed in ultra-high vacuum onto sputtered, single crystal ZnO(0001). These experiments indicate that adsorption of mercaptosilanes on sputter-cleaned ZnO(0001) occurs via the thiol group. On the nanocrystalline surface, which contains adsorbed hydroxyl groups, adsorption occurs via Si-O-Zn bond formation, but the possibility of adsorption on defect sites, via the thiol group, cannot be excluded and is suggested by the photoluminescence data.

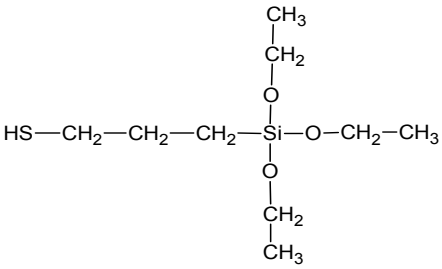
2. EXPERIMENTAL

2.1 Mercaptosilane and dodecanethiol adsorption

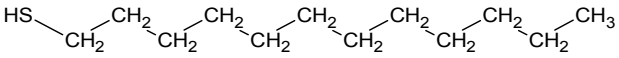
2.1.1 Chemical structures



3-mercaptopropyltrimethoxysilane



3-mercaptopropyltriethoxysilane



Dodecanethiol

2.1.2 Nanocrystalline ZnO. Nanocrystalline ZnO (nano-ZnO) nanorods (Nanocerox, Inc.) were vacuum-dried at 200°C overnight before use. As determined by transmission electron microscopy, the nanocrystalline ZnO rods were typically 10-20 nm wide and 100-300 nm long. The nano-ZnO was suspended in 95% ethanol/5% H_2O at pH 5 (adjusted with acetic acid) by means of sonication with a Branson Cell Disruptor. 3-mercaptopropyltriethoxysilane (MPTES, Gelest, Inc.) was added to the suspended solution (1/2.5 ZnO/silane on a weight basis) without further purification, and the mixture was allowed to react for 1 h at 75°C. The powders were collected by filtration and washed extensively with 100% ethanol. The samples were dried at 110°C for 10 min and stored in a desiccator. Samples for XPS were prepared by dispersing 60 mg of the nano-ZnO, or the silane-modified nano-ZnO, in 30 mL of the aqueous ethanol solution and agitating the mixture for 3 min with the cell disruptor. The sample was then poured onto a small copper coupon (1 cm^2,

pre-cleaned with dilute hydrochloric acid, methanol and distilled water) in a Gooch crucible. The solution was allowed to evaporate/drain through the crucible overnight at room temperature. This procedure resulted in a uniform coating of the nano-ZnO powder onto the copper coupons. These coated copper coupons were attached to XPS sample stubs using silver paint.

2.1.3 Single crystal ZnO(0001). A Zn-terminated ZnO(0001) single crystal from MTI Corporation was attached to a copper XPS sample stub using vacuum compatible, high temperature silver adhesive and loaded into the introduction chamber of a VG ESCALAB MKII photoelectron spectrometer. After extensive heating and outgassing at ca. 150°C, the ZnO single crystal was heated to 600°C and sputtered using 1000-5000 eV argon ions. The sputter cleaning was carried out in the preparation chamber of the instrument, which had a vacuum lower than 1 x 10^{-9} Torr. After cleaning, the sample was quickly moved to the analysis chamber, where the pressure was ca. 5 x 10^{-10} Torr. XPS was used to confirm sample cleanliness, and it was dosed with 3-mercaptopropyltrimethoxysilane (MPTMS, Gelest, Inc.) by admitting vapor through a variable leak valve. A nominal exposure of 50 L was used by dosing the ZnO(0001) at a pressure of 1 x 10^{-7} Torr for 500 sec. In order to confirm that thiols can adsorb to ZnO surfaces, sputter-cleaned ZnO(0001) was also dosed with 90 L of dodecanethiol (DDT, Sigma-Aldrich, Inc.) by leaking this vapor into the vacuum chamber at a pressure of 1 x 10^{-7} Torr for 900 sec. No corrections were made for ionization gauge cross sections in measuring these pressures. Several freeze-pump-thaw cycles had been used to purify the MPTMS and DDT, which were stored in glass reservoirs behind their respective variable leak valves, and residual gas analyses confirmed their purities. All adsorption experiments were performed with the sample at ambient temperature.

2.2 Photoelectron spectroscopy. MgKα ($h\upsilon$ = 1253.6 eV) radiation was used for XPS. Ejected photoelectrons were energy analyzed using a concentric hemispherical analyzer (CHA). Unless otherwise noted, a 90° take off angle (TOA, defined as the angle between the sample plane and a perpendicular to the entrance of the CHA) was used. For some XPS experiments, greater surface sensitivity was achieved by using a 20° TOA. Samples were electrically grounded for XPS measurements, and the binding energy scale is referenced to the Fermi level. No corrections for charging, which may result from positive charge buildup on the surface during XPS analysis and shift the spectra to slightly higher binding energy, have been made.

2.3 Photoluminescence and FTIR. Photoluminescence spectra of the powders were obtained in reflection mode using a Fluorolog 3 fluorescence spectrometer (Horiba Jobin Yvon, Inc) equipped with a solid sample holder accessory. A total of 3 scans were averaged for each sample. Infrared spectroscopy of MPTES functionalized nano-ZnO was performed with a BioRad Fourier transform infrared spectrometer (model FTS-60A). For these measurements, pellets were prepared using 200 mg of KBr and 15 mg of sample. A total of 32 scans were averaged for each sample using a pure KBr pellet as a reference.

3. RESULTS AND DISCUSSIONS

3.1 X-ray photoelectron spectroscopy

3.1.1 Adsorption of MPTES on nanocrystalline zinc oxide

Figure 1(a) shows XPS scans of the Zn3p/Si2p region of nano-ZnO and MPTES-functionalized nano-ZnO. The presence of the Si2p signal at 102.5 eV confirms covalent attachment of MPTES to the ZnO surface. Figure 1(b) contains corresponding C1s spectra. There are minimal differences between the spectra, with both showing a major peak at ca. 285.8 eV and a small peak at ca. 290.0 eV. In the case of the nano-ZnO control, the carbon signal at 285.8 eV is due to adventitious carbon, which is typically present on any sample that is not cleaned in ultrahigh vacuum. In the absence of surface charging (due to build-up of positive charge during XPS analysis), this usually appears at a lower binding energy (ca. 285 eV). This suggests that some surface charging is occurring. The very small higher binding energy peak at 290.0 eV in the control likely originates from adsorption of –COOH groups from the acetic acid used in the preparation of the nano-ZnO sample. The similarity in C1s intensities for the control and MPTES-functionalized samples suggests that silane adsorption replaces a portion of the adventitious carbon. The higher binding energy component in the MPTES-functionalized ZnO sample may be due to carbon atoms originating from residual unhydroxylated ethoxy groups.

Figures 2(a) displays corresponding O1s spectra before and after silane modification. The two O1s peaks at ca. 531.0 and 533.0 eV are assigned to bulk ZnO oxygen and surface hydroxyl species, respectively. This assignment is corroborated by data in Figure 2(a) for the sputtered single crystal ZnO(0001), which does not contain hydroxyl groups. The higher binding energy O1s shoulder in the 532-534 eV range is also assigned to surface hydroxyl groups based on XPS data in ref. 10.

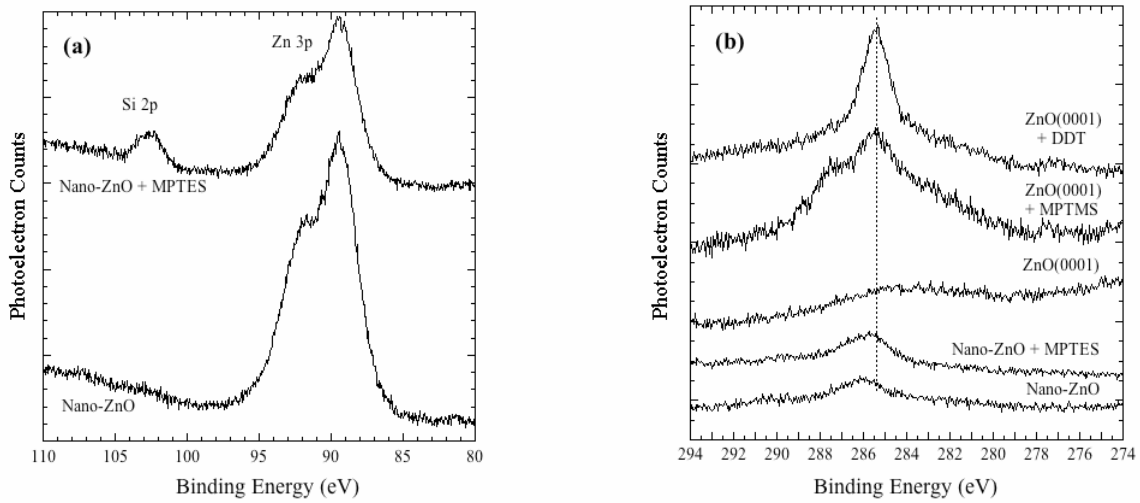


Figure 1: MgKα XPS of (a) the Zn3p and Si2p regions of nanocrystalline zinc oxide before and after functionalization with MPTES and (b) the C1s region of the same samples. Also included are C1s spectra of sputter-cleaned ZnO(0001) and the spectra that result from dosing with MPTMS and DDT.

Adsorption of MPTES causes growth of the higher binding energy O1s peak due to the formation of Zn-O-Si bonds and/or the presence of ethoxy groups. Figure 2(b) shows the S2p region of the MPTES-functionalized nano-ZnO surface. The observed peak binding energy of ca. 163.5 eV is consistent with intact thiol groups[13]. The presence of hydroxyl groups and low pH conditions used during the synthesis (pH=5) are expected to favor adsorption of MPTES via hydrolysis of the siloxy groups.[5,6] However, the XPS data alone cannot exclude the possibility of adsorption via the thiols, as will be discussed in more detail.

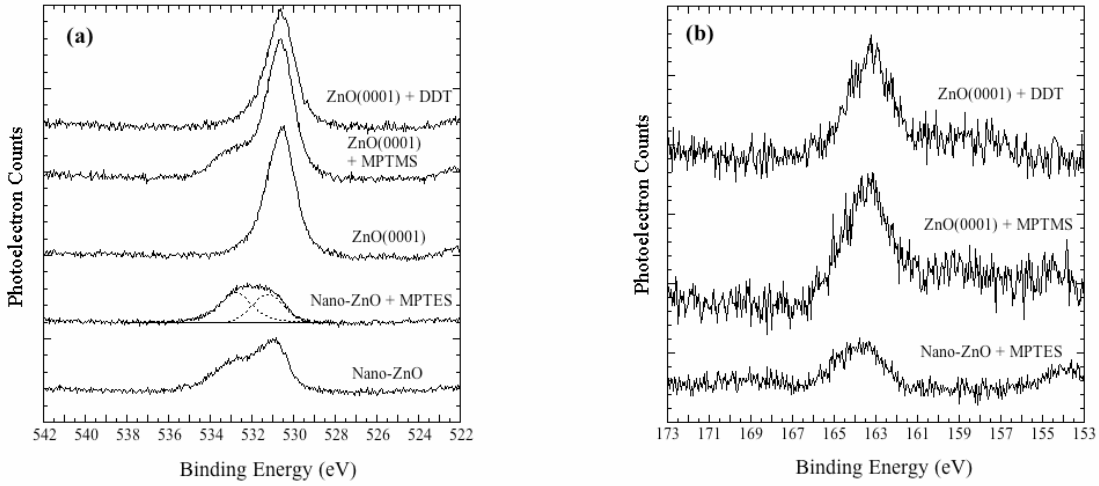


Figure 2: MgKα XPS of (a) the O1s region of nanocrystalline zinc oxide and sputter-cleaned ZnO(0001) before and after adsorption of MPTES, MPTMS, and DDT; (b) the S2p region of the samples following adsorption.

3.1.2 Adsorption of MPTMS and DDT on sputter-cleaned ZnO(0001)

Included in Figure 1(b) and Figures 2(a) and (b) are XPS spectra of ZnO(0001) that has been sputter-cleaned with 5000 eV argon ions prior to adsorption studies. Sputter cleaning results in removal of most of the adventitious carbon, as demonstrated in Figure 1(b). Adsorption of MPTMS gives rise to two overlapping C1s peaks centered at ca. 285.5 and

287.0 eV. The peak at 285.5 eV is due to C-C, C-S and C-Si species, while that at 287.0 eV arises from carbons bonded to oxygen atoms in residual methoxy groups, similar to conclusions drawn for MPTES on nano-ZnO. As shown in Figure 2, MPTMS adsorption on ZnO(0001) causes an O1s shoulder to the higher binding energy side of the main peak to emerge. The S2p peak from adsorbed MPTMS appears at 163.5 eV.

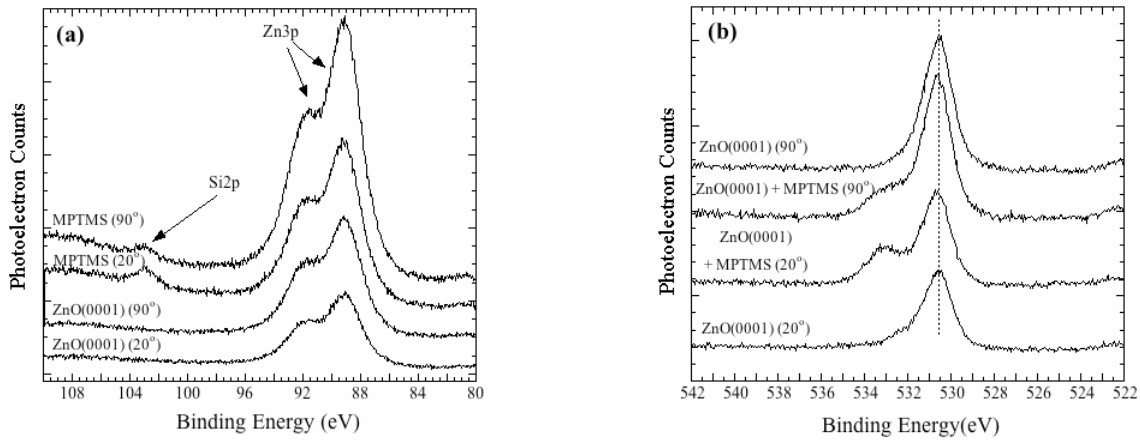


Figure 3: MgKα XPS using 90° and 20° take-off angles of the (a) Si2p and Zn3p regions and (b) O1s region of sputter-cleaned ZnO(0001) dosed with MPTMS.

As discussed in the introduction, MPTMS can, in principle, bond to ZnO(0001) either via Zn-O-Si or Zn-S bonding. The orientation of adsorbed MPTMS has been investigated by comparing XPS data taken with a 20° TOA to the 90° TOA data discussed above. The greater surface sensitivity in the case of the smaller TOA permits conclusions to be drawn as to how the MPTMS is adsorbed to ZnO(0001). Figure 3 shows angle-resolved XPS data of sputter-cleaned ZnO(0001) before and after MPTMS adsorption. As expected and illustrated in Figure 3(a), the intensity of the Si2p peak compared to the spin-orbit split Zn3p doublet increases as the take-off angle decreases. This is consistent with silicon being on top of ZnO(0001), which is the case regardless of which end of the molecule is bonded to the surface. However, the measured Si2p/S2p atomic ratio (spectra not shown) increases from 0.59 to 0.90 as the take-off angle decreases from 90° to 20°. This indicates that the silicon-containing silane groups reside closer to the sample/vacuum interface than the sulfur-containing thiol groups, consistent with bonding to the surface via the thiol groups.

In order to further investigate this, an experiment was performed in which a sputter-cleaned ZnO(0001) surface was dosed with dodecanethiol (DDT) by admitting its vapor into the ultrahigh vacuum chamber. Because of the use of a different sputter gun compared to the MPTMS studies described above, 1000 eV (instead of 5000 eV) argon ions were used for sample cleaning. No significant differences were observed in the cleanliness of the sample, although it is expected that the lower beam energy could result in slightly less surface damage. Figures 1 and 2 include C1s, O1s, and S2p XPS plots resulting from DDT adsorption. The C1s spectrum only exhibits a single peak (at 285.5 eV). This is in contrast to the MPTMS spectrum which contains a high binding energy shoulder due to intact methoxy groups. Similarly, in the case of DDT-dosed ZnO(0001), the O1s spectrum only has a single peak due to bulk zinc oxide while the MPTMS-dosed surface exhibits a high binding energy shoulder due to methoxy groups. Chemisorption of DDT to the ZnO(0001) surface is evidenced by the strong S2p signal. This persisted even after storage in the vacuum chamber for a week and heating at temperatures higher than 150°C.

Since no silane groups are present in DDT, these experiments convincingly demonstrate that bonding to sputtered ZnO(0001) is possible via thiol groups. The identical binding energy at 163.5 eV for the MPTMS and the DDT-dosed ZnO(0001) surface further suggests that both molecules bind to the surface in a similar fashion. A very similar S2p binding energy (164 eV) was reported for dodecanethiol adsorption *from solution* on zinc- and oxygen-terminated zinc oxide surfaces.[8] As discussed by the authors of ref. 8, the details of the bonding of the alkanethiol to the surface are unclear. The absence of higher binding energy S2p peaks argues against bonding of the thiol via oxidation and electron transfer to the surface. In the present work, adsorption of DDT was performed in ultrahigh vacuum following sputter cleaning. Sputtering is expected to create oxygen vacancies on the surface, and it might be expected that S-Zn bonding

would occur at the oxygen vacancies. However, the absence of substantial higher binding energy S2p signal in Figure 2(b) suggests that this is not the major mode of adsorption for either DDT or MPTMS.

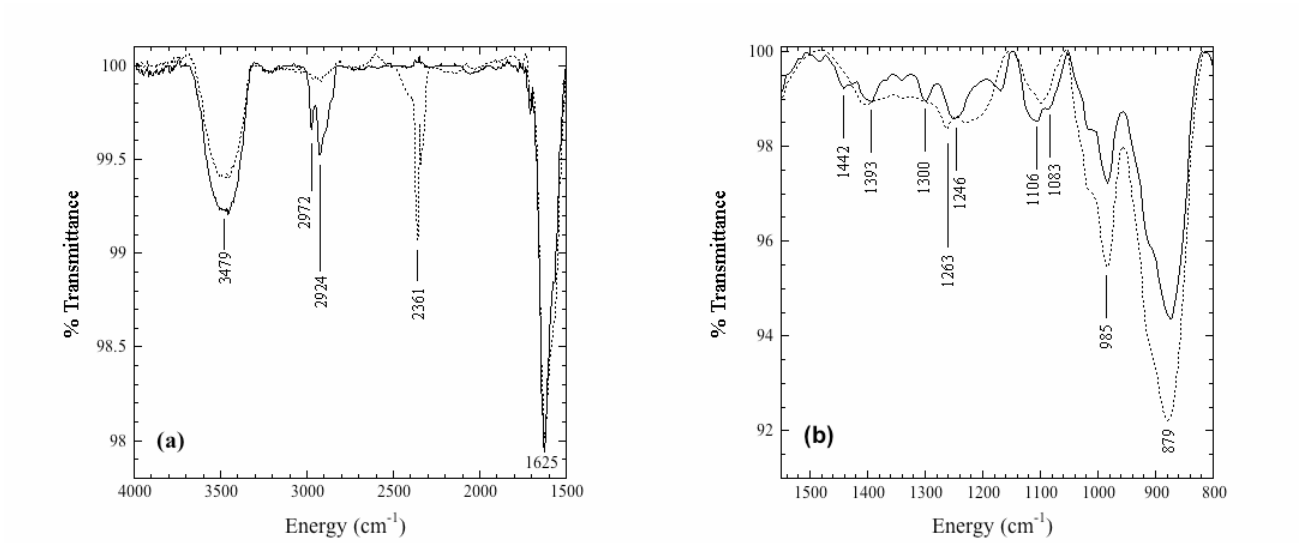


Figure 4: FTIR spectra of unfunctionalized (dashed curve) and MPTES-functionalized (solid curve) nanocrystalline zinc oxide in the range of (a) 4000-1500 cm^{-1} and (b) 1550-800 cm^{-1}.

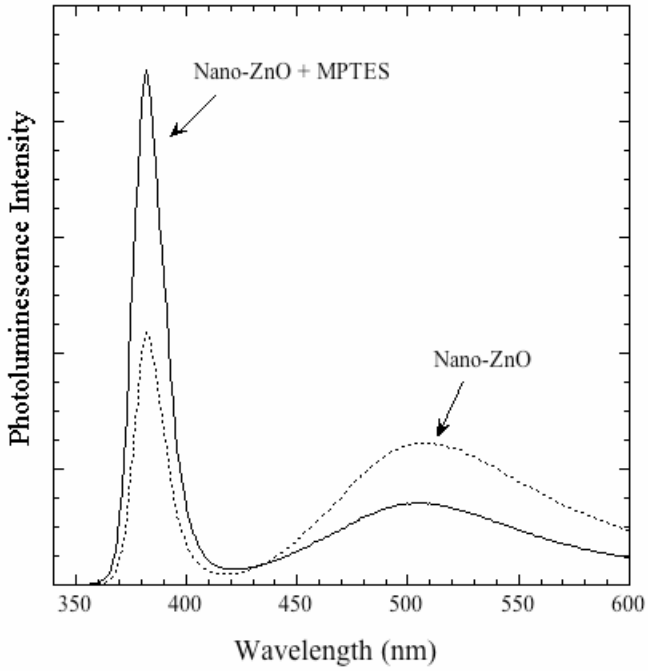


Figure 5: Photoluminescence spectra of unfunctionalized (dashed curved) and MPTES-functionalized nano-ZnO (solid curve) using an excitation wavelength of 325 nm.

3.2 FTIR and photoluminescence results

Figure 4 shows FTIR spectra of unfunctionalized and MPTES-functionalized nano-ZnO. Prior to functionalization, the particles exhibit vibrations consistent with adsorbed hydroxyl groups (band centered at 3479 cm^{-1}). Persistence in the intensity of this peak after MPTES functionalization indicates that not all of the hydroxyl groups on the surface are replaced by MPTES. However, evidence of MPTES bonding is provided by CH_3 and CH_2 peaks at 2972 and 2924 cm^{-1} and methyl bends at ca. 1393 cm^{-1}. The presence of the methyl peak substantiates the conclusion that ethoxy groups remain on the MPTES molecule following attachment to the surface. The peak at 2361 cm^{-1} may be due to adsorption of atmospheric carbon dioxide on Zn^{2+} vacancies,[14] although instrumental purging inefficiencies make this interpretation inconclusive. The large peak at 1625 cm^{-1} that remains relatively unchanged after adsorption is likely due to a carbonate species,[15] perhaps originating from the acetic acid used in the acidification of the zinc oxide. The absorbance peaks at 1106 and 1083 cm^{-1} arise from asymmetric stretches of Si-O-Si and Si-O-C, respectively.[16] The presence of Si-O-Si bridges indicates that polymerization of adjacent MPTES on the ZnO surface has occurred.

Figure 5 shows photoluminescence spectra of these samples. Functionalization with MPTES causes the visible emission peak centered at 510 nm to decrease in intensity and the UV peak centered at 380 nm to increase. The green peak is believed to originate from an electron decaying from an oxygen vacancy into a photoexcited hole.[4] The lower intensity due to MPTES adsorption on the nano-ZnO sample suggests that oxygen vacancies are passivated by MPTES functionalization. The MPTES-induced changes in photoluminescence differ from our previous investigations of nano-ZnO functionalized with 11-triethoxysilylundecal.[1] In this case, it was found that the visible emission peak was essentially unchanged while the UV peak doubled in intensity. This behavior was postulated to be due to adsorption that quenches surface-dependent nonradiative processes, funneling the energy into the UV emission peak. Such behavior is consistent with nonpassivation of lattice defects (i.e. oxygen vacancies). The different behavior in the present case suggests that lattice defect passivation occurs in the case of MPTES, perhaps via Zn-S bonding.

4. CONCLUSIONS

This work demonstrates that chemisorption of thiols occurs on ZnO(0001) when hydroxyl groups are absent, as evidenced by adsorption of dodecanethiol. Furthermore, bonding via the thiol end of a mercaptosilane occurs on sputtered ZnO(0001) dosed in ultrahigh vacuum, as indicated by angle-resolved XPS studies. In the case of solution adsorption of MPTES on nano-ZnO, the situation is more complicated. The low pH conditions and presence of surface hydroxyl groups are expected to favor adsorption of the molecule via a condensation reaction and the formation of Zn-O-Si bonds. However, it is possible that adsorption on surface defects may occur via thiol groups. Previous photoluminescence studies performed using 11-triethoxysilylundecal, which does not contain a thiol group, showed a different photoluminescence behavior than that observed in the present study. The photoluminescence results in the present case may be related to passivation of oxygen vacancies by MPTES adsorbed via S-Zn bonds. However, this is only speculation at this point. Experiments are in progress to determine whether or not MPTMS can bond to hydroxylated ZnO(0001) and to evaluate whether an alkanethiol can bond to hydroxylated nano-ZnO.

5. ACKNOWLEDGEMENTS

The authors acknowledge financial support of this research from the US Army Natick Soldier Research, Development & Engineering Center. This document has been approved for unlimited distribution (PAO #08-320).

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