Photoluminescence Properties of Surface-Modified Nanocrystalline ZnS : Mn

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DBS surface-modified nanocrystalline ZnS : Mn was prepared by a precipitation method. Photoluminescence spectra and decay curves were measured and compared to those of unmodified samples. For both kinds of samples, luminescence decay curves of 600 nm emission consist of two components with nanosecond (ns) and millisecond (ms) lifetimes. The nanosecond component is attributed to zinc vacancies luminescence, with peak located at 440 nm. While the millisecond component is attributed to Mn^{2+} luminescence and its decay time changes with Mn^{2+} concentration and surface modification. The surface-modified sample has a longer lifetime compared to unmodified samples. The photoaging of surface-modified samples is slow. Particle size effects on photoaging were also examined. For nanocrystalline ZnS : Mn photoaging is more noticeable than that of bulk material. After UV irradiation, photoluminescence intensity of the modified sample is several times larger than that of the unmodified sample, because the surface-active reagent decreases surface defects and depresses radiationless transitions. XPS yields direct evidence of the surface-modification effect on the surface structure. © 2000 Academic Press

Key Words: nanocrystalline; ZnS : Mn; surface modification; lifetime.

I. INTRODUCTION

In 1994, Bhagava *et al.* (1) first reported the preparation and photoluminescence properties of nanocrystalline ZnS : Mn. They found that the photoluminescence lifetime of the transition $^4T_1$-$^6A_1$ of Mn^{2+} in nanosize ZnS : Mn crystals was shortened by 5 orders of magnitude relative to the bulk material. The ultrashort lifetime, together with the high efficiency reported, made this kind of doped nanocrystals very attractive for optoelectronic applications (2). However, there were some controversial results for this kind of material. On the one hand, there was a report that the shortening of lifetime had been verified (3). On the other hand, this phenomenon was not observed for nanocrystalline

ZnS : Mn samples prepared by a pressure cycle method (4) or for nanocrystalline CdS : Mn samples prepared by an inverted micelle technique (5). Further research on this problem is needed. Bhagava *et al.* also reported the important effect of surfactants and UV curing on luminescent efficiency (1). In nanocrystals the ratio of particle surface area/volume is much larger than that in bulk material. For a nanocrystalline particle ZnS : Mn with a diameter of 2–3 nm, there are only 100–200 primitive cells and almost half of them are on the particle surface, so it is conceivable that the surface state, particularly surface defects, surface disorders, and surface void bands, will influence the luminescent properties of nanocrystalline ZnS : Mn. In this paper, photoluminescence (PL) emission spectra, decay time, and photoaging of nanocrystalline ZnS : Mn with and without surface modification were studied and compared with those of bulk ZnS : Mn.

II. EXPERIMENT

Nanocrystalline ZnS : Mn was prepared by coprecipitation. The process was as follows: first, aqueous stock solutions of $Zn(NO_3)_2$, $MnCl_2$, and Na_2S were prepared, and then $Zn(NO_3)_2$ and $MnCl_2$ solutions were mixed together according to certain doping concentrations. After that the precipitant solution Na_2S was added to the mixture drop by drop with vigorous stirring. The collected precipitate was washed and dried at 40°C for 24 h. In preparation of surface-modified ZnS : Mn^{2+} nanocrystalline, surfactant DBS (dodecyl benzene sulfonic acid sodium salt), alcohol, and benzene were added to the $Zn(NO_3)_2$, $MnCl_2$, and Na_2S aqueous solutions, respectively. The remainder of the process was the same. The resulting compounds appeared as a white powder. In order to obtain samples with different concentrations of Zn^{2+} vacancies, the ratio of $(Zn + Mn)/S$ was adjusted by controlling the quantity of precipitant Na_2S. Bulk powders of ZnS : Mn were prepared by the usual solid-state reaction.

The crystal structure was analyzed by use of a D/Max-rA X-ray diffraction apparatus. The diffraction pattern showed a typical zinc blende crystallographical structure. The particle size was estimated from the half-width of the peaks of the X-ray diffraction pattern, using the Scherrer equation. Particle size prepared

by coprecipitation was about 5 nm. The X-ray photoelectron spectra were recorded with a VG ESCAlab 5 multitechniques electron spectrometer.

Photoluminescence spectra were measured by a Jobin-Yvon monochrometer. The third harmonic of YAG : Nd laser (20 W Quantel) at 355 nm was used as excitation source. The signals were fed into a Stanford SR510 lock-in amplifier and detected by an R-374 Hamamatsu photomultiplier. PL decay times were measured by using a Lecroy 9410 oscilloscope interfaced with a computer. The photoaging curves were recorded with a GDM-1000 double grating monochrometer.

III. RESULTS AND DISCUSSION

A. Photoluminescence Spectra

The excitation peak of Mn^{2+} emission in nanocrystalline ZnS : Mn is located at 350 nm. The emission spectra of nanocrystalline ZnS : Mn without surface modification (sample A) are shown in Fig. 1. There are two broad bands; the orange band centered at 600 nm arises from the $^4T_1$-$^6A_1$ transition of Mn^{2+}, which is slightly red-shifted compared to the peak of bulk ZnS : Mn (6). The blue band peaks at 440 nm originate from the self-activated emission of Zn vacancies (7, 8). As the Mn^{2+} concentration increases, the relativity intensity of blue emission becomes small, showing that photoluminescence from the zinc vacancies and the Mn^{2+} is a competitive process. The emission spectrum of a surface-modified sample (sample B) is similar to that of sample A except that the intensity of B is about three to four times that of A. (Fig. 2)
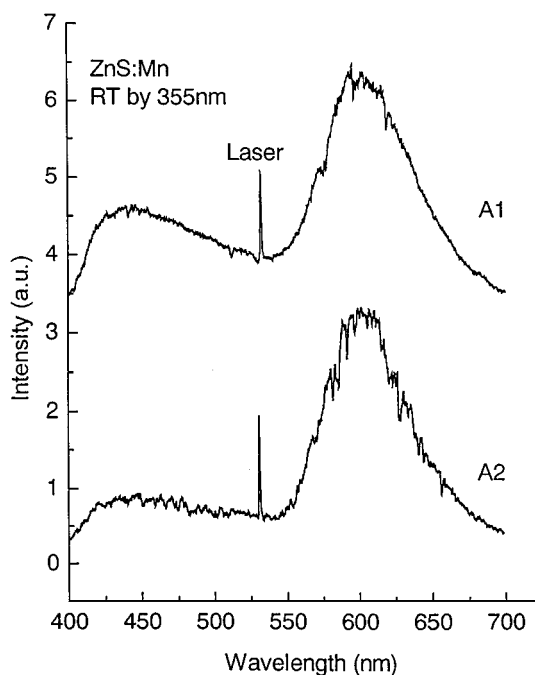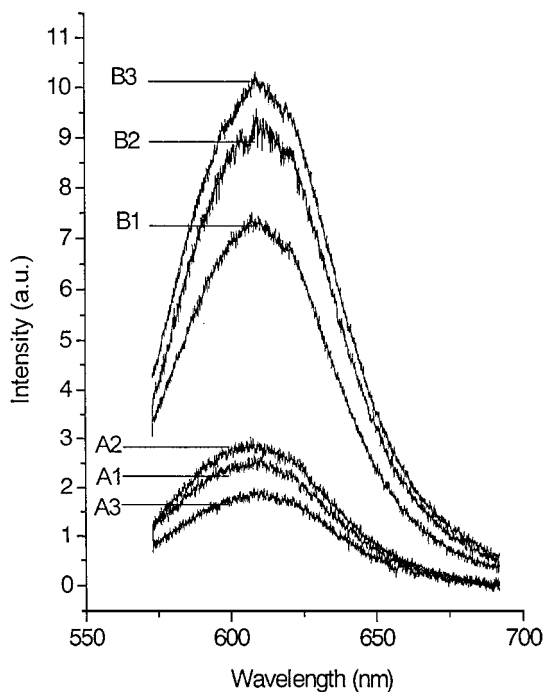

FIG. 2. The luminescence intensity of the orange band for normal nanocrystalline ZnS : Mn (A) and surface-modification samples (B) versus Mn^{2+} concentration (A1 and B1, 0.005 Mn; A2 and B2, 0.01 Mn; A3 and B3, 0.015 Mn).

B. Fluorescence Lifetime

Monitoring at a wavelength of 600 nm, a signal with a decay time less than 10 ns is detected (Fig. 3). Monitoring at 440 nm
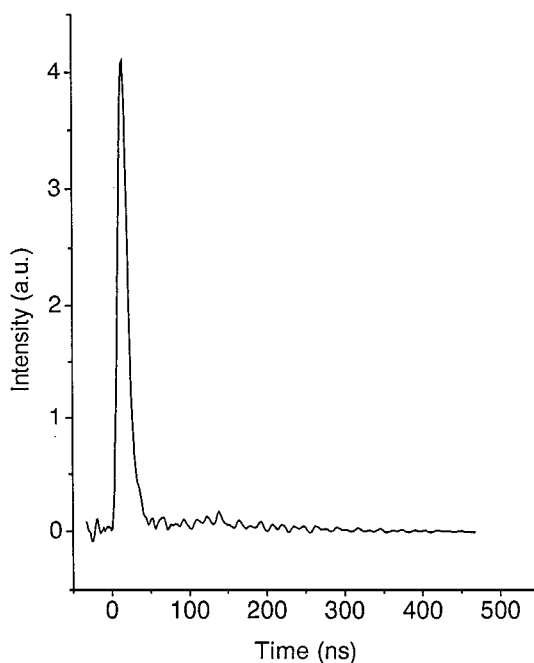

FIG. 1. Photoluminescence spectra of normal nanocrystalline (A) ZnS : Mn with different Mn^{2+} concentrations (A1, 0.005 Mn; A2, 0.01 Mn).

FIG. 3. Decay curves of nanocrystalline ZnS : Mn. Time scale of the oscilloscope was set at the nanosecond scale and the luminescence detected was at 600 nm.

gave a similar decay curve. No difference is found in samples with different Mn^{2+} concentrations and surface modifications. If the detected wavelength is changed from 600 nm to lower energy direction, the signal intensity decreases. But when the monitoring wavelength is changed in the other direction, to less than 600 nm, a stronger signal is observed. The signal intensity increases when the wavelength decreases and reaches a maximum intensity around 440 nm. This trend is similar to the zinc vacancy emission spectrum in Fig. 1, showing that the ns emission comes from the zinc vacancy luminescence, which occurs over a wide wavelength range.

However, when the measuring range was set at the millisecond scale and the monitoring wavelength at 600 nm, the decay curves were observed only when higher amplification was used. This is because although the integrated intensity of the millisecond component from the slow process is high, its instantaneous intensity is low. The decay curves of samples prepared under different conditions are shown in Fig. 4. The higher the Mn^{2+} concentration, the shorter the decay time. The decay times for samples modified with the surface-active reagent DBS are longer than those not modified. The decay curves could be well fitted by two exponential components (Fig. 5). Decay times of the samples are shown in Table. 1. The results are similar to the results for bulk ZnS : Mn (9). It is clear that ms decay consists of two processes, due to transitions of Mn^{2+} signal ions and Mn^{2+} coupled pairs, respectively (9). There are significant changes between bulk and nanocrystalline material. For bulk material the lifetime

FIG. 5. The decay curve of ZnS : 0.01 Mn. (—, fitting curve; ●, experiment curve).

is about 1.8 ms, while for nanocrystalline it is less than 1 ms. Changing the detection wavelength, either longer or shorter than 600 nm, the millisecond emission signal intensity becomes weaker.

Considering that the blue emission overlaps with the orange emission arising from the $^4T_1$-$^6A_1$ transition of Mn^{2+}, we can conclude that the nanosecond component detected at 600 nm comes from the blue emission, which is associated with the zinc vacancies. The Mn^{2+} luminescence has only a millisecond component. This statement is supported by other experiments: for example, in the samples for which S^{2-} is absent, blue emission is weak. If Zn/S were much larger, the blue emission would disappear totally and consequently there would be no nanosecond component in the decay curve of 600 nm emission.

On the other hand, the nanosecond component is not observed for bulk ZnS : Mn due to the fact that the blue emission centered at 440 nm is weak in bulk ZnS : Mn. As stated before, the ratio of particle surface area to particle volume in nanocrystalline ZnS : Mn is much larger than that in bulk
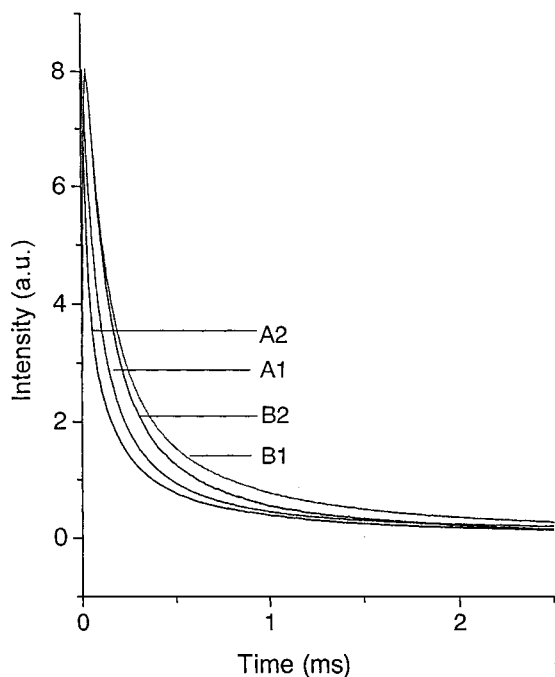

FIG. 4. Decay curves of nanocrystalline ZnS : Mn with different Mn concentrations (A1 and B1, 0.005 Mn; A2 and B2, 0.01 Mn) and different surface-modified samples (A, not modified; B, surface modification). Time scale of the oscilloscope was set at the millisecond scale and the emission detected was at 600 nm.
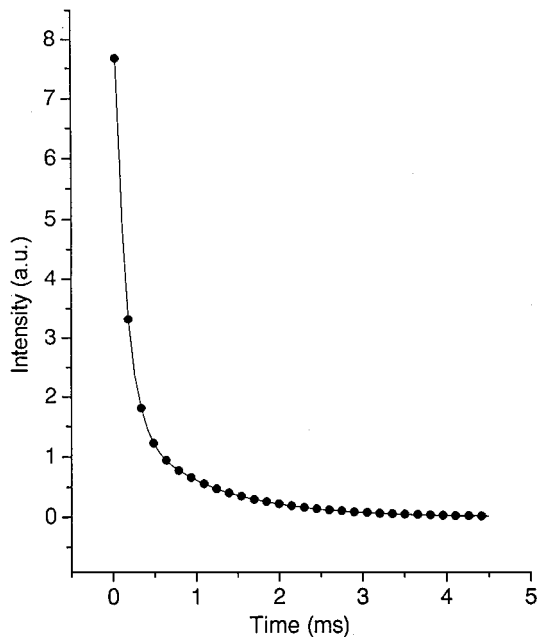
TABLE 1
Decay Times of Nanocrystalline ZnS : Mn

	Surface-modified nanocrystalline		Normal nanocrystalline	
	ZnS : 0.005 Mn	ZnS : 0.01 Mn	ZnS : 0.005 Mn	ZnS : 0.01 Mn
Time 1 (ms)	0.971	0.846	0.798	0.657
Time 2 (ms)	0.131	0.130	0.072	0.096

ZnS : Mn. A particle of nanocrystalline ZnS : Mn having a diameter of 2–3 nm contains only 100–200 primitive cells, in which almost half of the primitive cells are located at the particle surface, where many defects and void bonds exist. When the ratio of Zn/S is less than one, a large part of zinc vacancies appears at the particle surface, and the blue emission coming from the zinc vacancies can be observed. When the ratio of Zn/S is very large, it is difficult to record the blue emission, because the number of zinc vacancies is small. For bulk ZnS : Mn, the lattice vacancies distributed in one particle, on an average, are much less abundant than that in nanocrystalline material, and therefore the number of vacancies at the surface is fewer. We know that the surface-active reagent DBS modifies the nanocrystalline surface, leading to fewer void bonds. But it cannot decrease the zinc vacancies, so we still can see the emission with nanosecond decay times for the surface-modified samples.

The difference of lifetime between bulk and nanocrystalline material could be ascribed to surface defects. There are more defects in nanocrystalline than in bulk ZnS : Mn. The energy of excited Mn^{2+} transfers to surface defects in nanocrystalline more easily than in the bulk materials, so the lifetime of Mn^{2+} in nanocrystalline is shorter than that in bulk ZnS : Mn. Because the millisecond emission comes from the transition of Mn^{2+}, the difference of decay time at different Mn^{2+} concentrations and for different surface-modified samples is easy to understand. With increasing Mn^{2+} concentration, energy transfer increases, leading to a shorter decay time. When the surface-active reagent DBS is added to the reaction system, the DBS modifies the nanocrystalline surface, which results in fewer defects and a longer decay time.

C. Photoaging Curves

There always exists photoaging in ZnS : Mn-type phosphors. ZnS will decompose and separate out Zn when exposed to UV light, which results in decreasing emission intensity. We measured the photoaging of nanometer samples A and B and bulk sample C of ZnS : Mn. When exposed to the 365-nm UV light, these three kinds of samples all photoage and the color of the samples changes. The color of sample A became violet, sample B became light yellow, and sample C became gray. The emission intensity of Mn^{2+} versus time (photoaging curves) is shown in Fig. 6. We can find from that the following.

1. The initial luminescence intensities of the three samples are almost the same, which shows that although the grain size and the surface-modifying condition of the three samples are different, their luminescence efficiencies are almost the same. The initial luminescence intensity of sample B is the minimum. It may be caused by surface-active reagent, which decreases the absorbency of exciting light.

2. The three samples all suffer photoaging effects. For nanometer samples the photoaging process is very quick. In
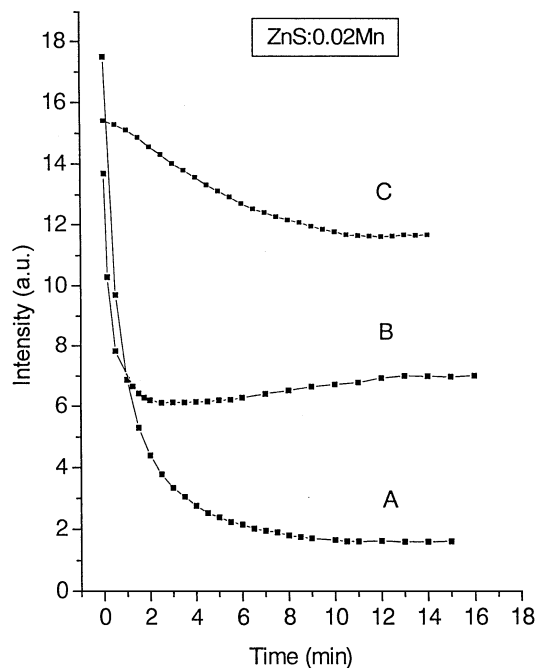

FIG. 6. Photoage curves of different samples: A, normal nanocrystalline; B, surface-modified nanocrystalline; C, bulk material.

less than 1 min, the intensity of sample B decreases 50% and that of sample A decreases to 30%. Then a much slower process occurs, and the intensities approach stable values.

3. Sample C has a slower photoaging process. The aging tendencies of samples A and C are same, and they become stable in 10 min.

4. There is a unique elevation process in the photoaging of sample B: When exposed to UV irradiation, the PL intensity decreases to a minimum in 3 min, then rises slowly, and reaches a stable value in 12 min.

5. The stable luminescence intensity of sample C is highest and that of sample B is half of that of sample C, and the luminescence intensity of sample A, the lowest, is about one-sixth that of sample C.

Photoaging arises from the photodecomposition of ZnS, due to the interaction of photon and materials. At first this reaction happens mainly at the particle surface, since the structure there is not stable. The larger the surface area, the more UV radiation absorbed, and the more extensive photoaging will be. For the same amount of ZnS, the nanometer sample has a larger surface area so it will suffer serious photodecomposition, which results in rapid initial variations in samples A and B. The further decomposition occurs in the inner part of the particle. Therefore the size of the particle is not important in the slower photoaging process. After UV irradiation, the different colors for different samples can also be explained. The decomposed metallic zinc is black. Sample A is the most unstable, and the amount of decomposed zinc is greatest, so its color is violet; the color of sample C is the metal zinc's color; for sample B metal

zinc is covered by the surface-modified reagent and shows light yellow.

In the photoaging curve of modified nanocrystalline sample the initial quick drop is smaller. This indicates that the surface-active reagent DBS added to the reaction mixtures is absorbed at the surface. This surface treatment suppresses channels of radiationless energy transfer and decreases the reactivity of photodecomposition, so the initial photoaging process is slowed. At the same time, DBS reacts with the nanocrystalline ZnS : Mn, which may recover some luminescence centers and result in the slight increase of PL intensity. The photoaging curve of sample B can be thought of as a superimposition of two opposite processes (Fig. 7): the photoaging curve of sample A in Fig. 6 (curve 2) and the later part of the surface modification (curve 3).

D. X-Ray Photoelectron Spectra

Using a X-ray photoelectron spectrometer, the state of atoms on the surface of the particles was analyzed. The XPS spectra of the S 2p electron of the surface-modified ZnS : Mn sample was obtained (Fig. 8), For comparison, the normal nanocrystalline ZnS : Mn was also measured under the same conditions. The XPS of normal samples has only one peak at 165.2 eV, as reported in (8). But there are two main peaks for surface modified samples: 166.1 and 172.3 eV. The two main peaks for surface-modified samples originate from the 2p electron in the core of nanocrystalline ZnS : Mn and the capping layer. In
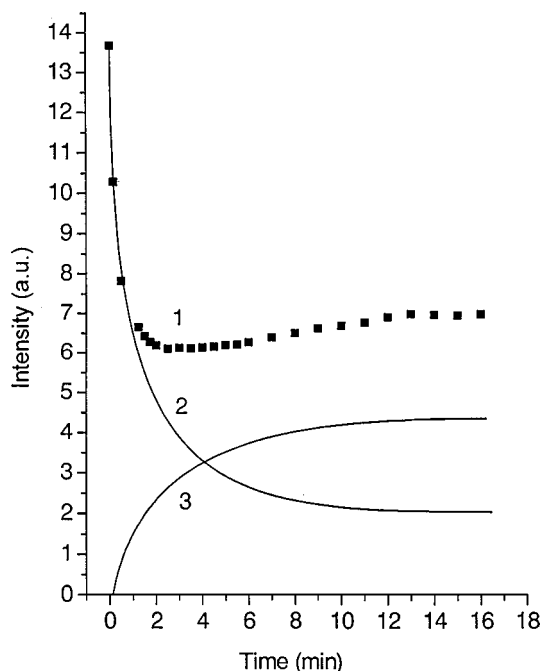

FIG. 8. XPS of normal nanocrystalline ZnS : Mn (A) and surface-modified sample (B).

addition, we can see that the S 2p binding energy of surface-modified samples (166.1 eV) is higher than the normal nanocrystalline ZnS : Mn (165.2 ev), showing that the surface of the modified sample is more stable than that of the unmodified samples. This difference of surface-modified and normal ZnS : Mn is attributed to the capping layer of DBS. During UV irradiation, the DBS reacts with the ZnS : Mn on the surface, making the bonding between Zn and S more stable. The results also confirm the conclusion about millisecond lifetimes and photoage curves. The XPS gives direct evidence of the surface-modification effect on the surface structure of nanocrystalline ZnS : Mn.

IV. CONCLUSION

Photoluminescence spectra, decay times and photoaging curves of surface-modified nanocrystalline ZnS : Mn were measured and compared to those of unmodified samples. The surface-modified sample has a longer lifetime than the normal samples. The photoaging process of surface-modified samples is slow. The effect of particle size on photoaging is also examined. Photoaging of nanocrystalline ZnS : Mn is more serious than that of bulk samples. After UV irradiation, the photoluminescence intensity of the modified samples is three times larger than for unmodified surfaces. The luminescence decay curve of 600 nm emission of nanocrystalline ZnS : Mn has two components with nanosecond and millisecond lifetimes, respectively. The nanosecond process was attributed to zinc vacancy luminescence with a peak located at 440 nm, while the millisecond process originates from the Mn^{2+} luminescence. The XPS give

FIG. 7. Photoage curve of surface-modified nanocrystalline Zns : Mn: superposition by photoage effect of normal nanocrystalline and effect of the surface modification. 1, photoage curve of modified nanocrystalline ZnS : Mn, 2, photoage curve of normal nanocrystalline ZnS : Mn; 3, effect of surface modification.
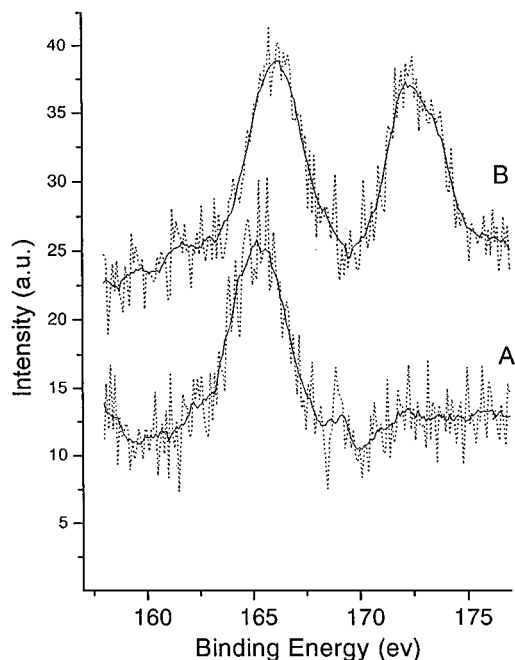
direct evidence of the surface-modification effect on the surface structure.

REFERENCES

1. Bhagava, R. N., Gallagher, D., Hong, X., and Nurmikko, A., *Phys. Rev. Lett*. **72,** 416 (1994).
2. Bhagava, R. N., *J. Lumin.* **70,** 85 (1996).
3. Sooklal, K., Cullum, B. S., Angel, S. M., and Murphy, C. J., *J. Phys. Chem.* **100,** 4551 (1996).
4. Kobayashi, M., *Phys. Status Solidi B* **198,** 515 (1996).
5. Chamarro, M. A., Voliotis, U., Grousson, R., Lavallard, P., Gacoin, T., Counio, G., Boilot, J. P., and Cases, R., *J. Cryst. Growth* **159,** 853 (1996).
6. Soo, Y. L., Ming, Z. H., Huang, S. W., Kao, Y. H., Bhagava, R. N., and Gallagher, D., *Phys. Rev. B* **50,** 7602 (1994).
7. Becker, W. G., and Bard, A. J., *J. Phys. Chem.* **87,** 4888 (1983).
8. Khosrari, A. A., Kundu, M., Jatwa, L., and Deshpande, S. K., *Appl. Phys. Lett.* **67,** 2702 (1995).
9. Busse, W., Gumlich, H. E., Meissner, B., and Thsis, D., *J. Lumin.* **12/13,** 693 (1976).
10. Xu, J., and Ji, W., *J. Mater. Sci. Lett.* **18,** 115(1999).