Enhancement in the photocurrent of ZnO nanoparticles by thermal annealing

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Abstract

The optoelectrical characteristics of the ZnO nanoparticles (NPs) annealed in vacuum or oxygen condition from 200 °C to 600 °C were examined. Increased on-off ratio (or, the ratio of photocurrent to dark current) was observed when they were annealed at 300 °C, 400 °C and 500 °C with the values enhanced about 4 orders compared to the as-prepared ZnO NPs in both annealing conditions, while the maximum efficiency was shown at the annealing temperature of 600 °C for the ZnO NPs annealed in vacuum with the value of 29.8 mA/W and at the temperature of 500 °C for those annealed in oxygen condition with the value of 40.3 mA/W. Photoresponse behavior of the ZnO NPs annealed in oxygen showed the sharp increase right after the ir exposure to the light followed by the slow decay and saturation during steady illumination, differing from the ZnO NPs annealed in vacuum which only exhibited the gradual increase. This difference occurred due to the curing effect of the oxygen vacancies. SEM images indicated no change in their morphologies with annealing, indicating the change in their internal structures by annealing, and most remarkably at 600 °C. As for their photoluminescence(PL) spectra, the decrease of the deep-level(DL) emission was observed when they were annealed in oxygen at 400 °C, and not at 200°C and 600 °C.

Key words: Optoelectrical characteristic, Zinc oxide nanoparticle, Annealing, Photoresponse

I. Introduction

ZnO has been a center of attention as a very useful material for UV detection with its beneficial characteristics such as large binding energy (60 meV) and wide band gap (3.37 eV) [1-6]. Its performance as UV detector is known to improve when oxygen molecules are adsorbed onto its surface, because desorption of the chemiadsorbed oxygen ions under illumination allows the electrons that were taken by the adsorbed oxygen to be released and deplete the holes created from electron-hole pairs generated by illumination [7-9]. Meanwhile, many studies were performed on the effect of annealing temperature and ambient condition for ZnO [10-13]. These results revealed that annealing of ZnO produces more vacancies on the surface as well as in the inner part with their density varying depending on annealing temperature. Therefore, when ZnO is annealed in oxygen condition, the increased number of oxygen is adsorbed on its surface and have more defects filled up inside. These results give the clue on how to

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maximize its characteristics to be used as UV detection. Despite this fact, not many studies focused on examining their optoelectrical characteristics with different annealing conditions in oxygen condition. In this study, we examined the optoelectrical characteristics of ZnO annealed in oxygen condition and compared to the ZnO annealed in vacuum to observe the effect of annealing temperature. As for its dimension, NPs were used because they were expected to produce more favorable results for UV detection with a large on-off ratio or the improved absorption of light.

II. Experimental

Gold electrodes separated by 20 μm were patterned by photolithography and thermal evaporation on a Si substrate. 1 g of ZnO NPs (purchased from Sigma Aldrich co.) with an average diameter of 70 nm was dispersed in 20 ml methanol to be cast between the electrodes. Samples were annealed for 1 h in vacuum or oxygen at the various temperatures from 200 °C to 600 °C. Photocurrent, photoresponse and PL were measured at room temperature in air.

The light source for photocurrent, photoresponse and PL spectra was the He-Cd laser of the 325 nm wavelength with the optical power of 10 mW, and photocurrent and photoresponse were detected by an Agilent 4155C semiconductor parameter analyzer while PL intensities were recorded by an InGaAs detector equipped with a monochromator (SPEX 1000M).

III. Results and Discussion

Figure 1 shows the photocurrent characteristics of the as-prepared ZnO NPs. The I-V characteristics of the dark current and photocurrent are both ohmic. The on-off ratio and efficiency are 1.94 x 10^2 and 0.49 mA/W at 2.5 V.

The on-off ratio and efficiency of the ZnO NPs annealed at various temperatures in vacuum or oxygen condition are presented in Table. 1 and plotted in Fig. 2. We observe in Fig. 2(a) that the on-off ratio is larger when ZnO NPs are annealed at 300 °C, 400 °C, 500 °C in both annealing conditions with their values increasing from 6.53 x 10^5 to 2.24 x 10^6 times that of the as prepared ZnO NPs while it is relatively smaller for the ZnO NPs annealed at 200 °C and 600 °C. The reduction of the on-off ratio when annealed at 600 °C is due to the sudden increase of the dark current. On the other hand, the efficiency is calculated to be maximum at the annealing temperature of 600 °C with the value at 29.8 mA/W when ZnO NPs are annealed in vacuum, and in case of annealing in oxygen, the magnitude is largest with 40.3 mA/W at 500 °C. The efficiency tends to improve as the annealing temperature increases in vacuum condition, but when they was annealed in oxygen, this tendency is changed with its largest value at the annealing

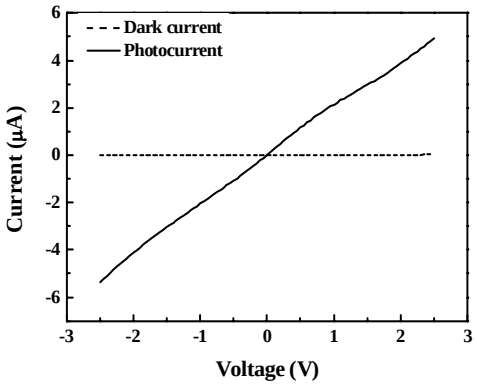

Fig. 1. Dark current and photocurrent (excited by the 325 nm wavelength light) plotted as a function of the applied voltage for the ZnO NPs.

Table 1. The ratio of the photocurrent to the dark current (or, on-off ratio) and efficiency of the annealed ZnO NPs in vacuum and oxygen under the illumination of light with the 325 nm wavelength.

	on-off ratio		efficiency	
ambient / Temperature	vacuum	oxygen	vacuum	oxygen
200 °C	$0.33x10^4$	$1.44x10^4$	2.24	4.27
300 °C	$2.39x10^6$	$1.87x10^6$	4.96	8.1
400 °C	$6.53x10^5$	$1.23x10^6$	8.74	16.5
500 °C	$2.24x10^6$	$9.98x10^5$	13.5	40.3
600 °C	$2.75x10^2$	$4.51x10^4$	29.8	34.4

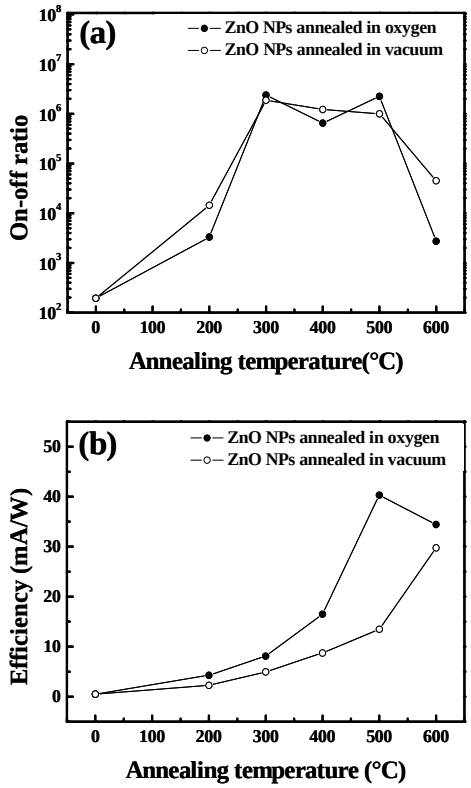

Fig. 2. (a) On-off ratio and (b) efficiency of the ZnO NPs plotted as a function of the annealing temperature under the illumination of 325 nm light at a bias voltage of 2.5 V.

temperature of 500 °C and the value decreasing at the higher annealing temperature of 600 °C.

The annealing effect on the photocurrent of the ZnO NPs is related to the oxygen vacancies on the surface. When the oxygen vacancies increase on the surface, more oxygen molecules in air are supposed to adsorb on them, contributing to the increase of the photocurrent. The relation between the density of the surface oxygen vacancies and annealing temperature has been examined in a few reports [14-15]. They reported that the annealing treatment of ZnO at the temperatures higher than 300 °C leads to the remarkable increase of water adsorption into ZnO with the strikingly reduced angle of the water drops on the surface. Considering that both water and oxygen molecules have the tendency to coordinate into the oxygen defect sites, this result is applicable to oxygen molecules. The similar result was reported for TiO_2 on which the water absorption increase was spotted at the higher temperature than 227°C. From these results, the critical temperature that brings the noticeable change on the surface of ZnO and TiO_2 is noticed between 200°C and 300°C and the effect became severe with increasing annealing temperature. In this study,we observe that the on-off ratio becomes very large at the annealing temperature of 300 °C, 400 °C and 500 °C averaging an increase of 4 orders from the as prepared ZnO NPs, and also the efficiency values increase compared to the as prepared ZnO NPs. This result is in very good agreement of the references [14-15] which mentioned the increase of surface vacancy effect at the higher annealing temperature than 300 °C and this is also supported by the smaller magnitude of the on-off ratio at the annealing temperature of 200 °C that was caused by the insufficient thermal energy at the temperature.

As for the annealing temperature of 600 °C, the efficiency decreases compared to those annealed at 500 °C for the ZnO NPs in case of the oxygen annealing condition, while that of the ZnONPs annealed in vacuum still increases. Therefore, the difference of the efficiencies between the ZnO NPs annealed on vacuum and oxygen is reduced at 600°C, showing a very little gap between them. The increase of the XRD peak along the c-axis (0002) is known to be remarkably enhanced with the higher annealing temperature than 600 °C, so that along with the increase of the dark current when annealed at 600 °C shown above, it can be possibly assumed that annealing of ZnO NPs at 600 °C possibly brings the change to the optoelectrical characteristics of the ZnO NPs. This characteristic was cautiously observed for the other experiments shown below.

Figure 3 presents the photoresponse of the ZnO NPs annealed at (a) 200 °C, (b) 400 °C and (c) 600 °C as a function of time at a bias voltage of 1 V. It is notable that the large difference is shown between the ZnO NPs annealed in vacuum and oxygen at 400 °C, differently from the ZnO NPs

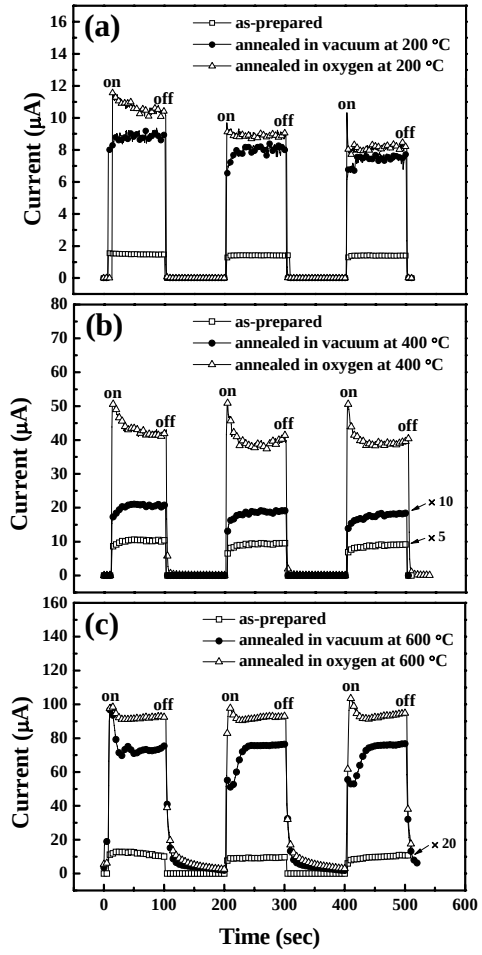

Fig. 3. Magnitudes of the photocurrent plotted as a function of time when the light with the wavelength of 325 nm was switched on and off at the bias of 1 V to the ZnO NPs annealed at (a) 200 °C, (b) 400 °C and (c) 600 °C in different ambient conditions.

annealed at 200 °C that exhibited the ignorable difference between the ZnO NPs annealed in two conditions. The result shows the thermal energy effect mentioned in Table. 1and Fig. 2.

The photocurrent of the ZnO NPs annealed in vacuum exhibits the steady increase as time passes by just as the as prepared ZnO NPs. This behavior matches the usually known characteristic of ZnO. The steady increase of the photocurrent under illumination has been revealed to be mainly concerned with trap sites; i.e, when some electrons fall into the trap sites formed by oxygen vacancies, they either recombine with the photo-generated holes or are detrapped back to the conduction band by overcoming the energy barrier. The increase of the photocurrent is explained by the dominance of the electrons that overcome the barrier over the ones that recombine. Thus, this behavior of the ZnO NPs annealed in vacuum is understandable considering its nature to produce oxygen vacancies. On the other hand, ZnO NPs annealed in oxygen shows the sharp increase of the current right after they are exposed to the light and the slow decay and saturation afterwards. This behavior is a unique characteristic distinguished from the ZnO NPs annealed in vacuum and from this fact, it is induced that this behavior is due to the curing effect of oxygen. The curing of those vacancies reduces the number of trap sites the electrons fall into, and this increases their lifetime. Owing to this increased lifetime, the density of charge carriers increases and the photocurrent improves. This effect is severe and the initial magnitude of the photocurrent is so huge. As for the gradual decay of the photocurrent after this sharp increase, there are some possible explanations but the most reasonable one is that some of oxygen are desorbed incompletely from the surface and readsorb onto the surface under illumination. These readsorbed oxygen molecules take the free electrons, leading to the decrease of the current.

In calculating the time constant, we took three stages of the photoresponse into account. The rising times for the ZnO NPs annealed in vaccum or oxygen are both within 1 s except the ZnO NPs annealed in oxygen at 600 °C, which shows the rise time constant τ=1.9 s. The decay time constants are divided into two stages, which are the fast decay process and the secondary subsequent process. The fast decay processes exhibits the decay time constants all within 1 s just as the rising times, and the subsequent decay times are 13.5 s, 2.8 s, 48.5 s for the ZnO NPs annealed at 200 °C, 400 °C and 600 °C in vacuum and 21 s, 4.5 s, 3.8 s for the ZnO NPs annealed at 200 °C, 400 °C and 600 °C in oxygen, respectably. The short response time for

the rise and decay time is due to the generation and recombination of the electron-hole pairs and the slow secondary decay time is caused by the readsorption of the oxygen molecules. It was reported that the longer subsequent decay time is induced by the reduced rate of the oxygen readsorption onto the surface of ZnO, which usually occurs when the surface coverage rate is so high [16]. ZnO NPs annealed in vacuum have more vacancies on their surfaces than the ZnO NPs annealed in oxygen, so that the subsequent decay time is reduced for them when the light is switched off.

The SEM images for the ZnO NPs annealed at 200 °C, 400 °C and 600 °C are displayed in Fig. 4. These images indicate that there is almost no change in their morphologies at all the annealing temperatures. This indicates that the change in their optoelectrical characteristics is mostly concerned with the change in their internal structures instead of the interaction between the particles. To examine this further, we investigated the PL spectra of the ZnO NPs.

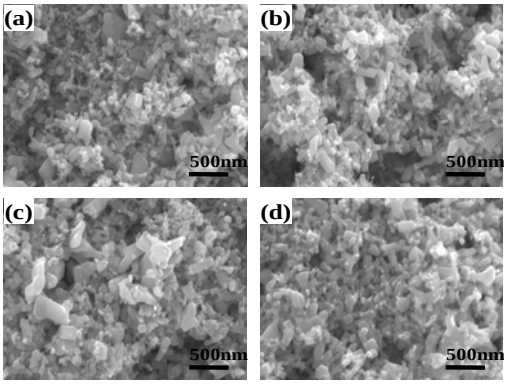

Fig. 4. SEM images of the ZnO NPs (a) as prepared and annealed at (b) 200 °C,(c)400°C and (d) 600 °C in oxygen condition.

Figure 5 shows the PL spectra of the ZnO NPs as prepared and annealed at various temperatures in vacuum or oxygen condition. It is presented in Fig. 5(a) that the PL spectra of the as prepared, vacuum and oxygen annealed ZnO NPs exhibited an ignorable difference in their values when they were annealed at 200 °C, while the plunge of the deep-level(DL) emission at the wavelength of about

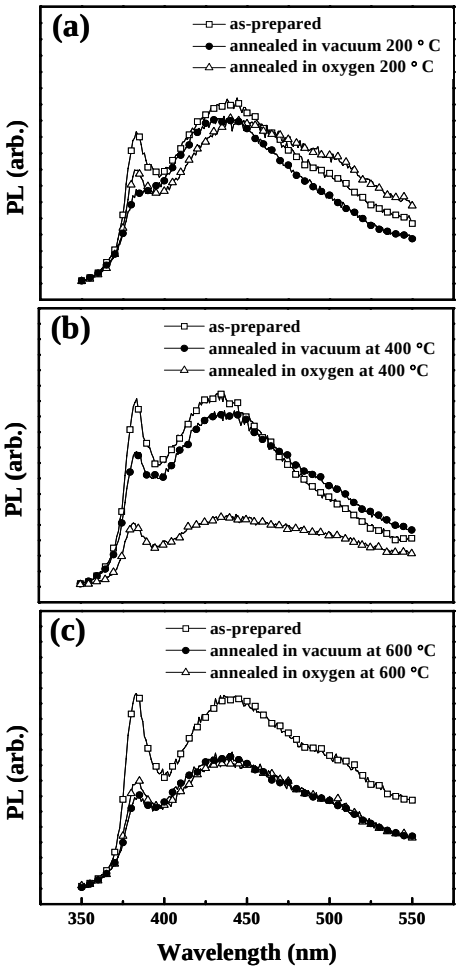

Fig. 5. PL spectra of the ZnO NPs when they were annealed at (a) 200 °C, (b) 400 °C and (c) 600 °C in different ambient conditions under the illumination of the light with the 325 nm wavelength.

450 nm appeared for the ZnO NPs annealed at 400 °C in oxygen in Fig. 5(b). This plunge of the DL emission peak has something to do with the increase of the oxygen vacancies on the surface and in the inner part by annealing, because the DL emission of ZnO is caused by the oxygen vacancies which have the wavelength at around 450 nm. Thus, the peak at this wavelength decreases when

the vacancies are filled up. This result is in agreement with Fig. 2, showing the relation between the photocurrent and PL spectra. The curing of the oxygen vacancies leads to the increase of the photocurrent, so when the largest photocurrent is observed, the drop of the PL spectra at the wavelength of 450 nm is also largest. For the ZnO NPs annealed at 600 ℃, the decrease of the DL peak was not shown differently from those of the ZnO NPs annealed at 400℃. The different optoelectrical characteristic was expected from Table 1. It suggests that annealing of ZnO at the high temperature reduces the curing effect of the defects even though it is done in oxygen condition, and from the result we obtained, this PL spectra behavior is assumedly concerned with the improvement of the crystalline.

IV. Summary

We have examined the photocurrent characteristics of the ZnO NPs annealed in vacuum or oxygen condition at the various annealing temperatures from 200 to 600 ℃. The on-off ratio and efficiency are 1.94×10^2 and 0.49 mA/W for the as prepared ZnO NPs, respectably. The on-off ratios are enhanced from 6.53×10^5 to 2.24×10^6 times those of the as-prepared ZnO NPs at the annealing temperatures of 300 ℃, 400 ℃ and 500 ℃ in both photoresponse, the ZnO NPs annealed in oxygen shows the sharp increase right after exposure to the light and gradual decrease and saturation process during the steady illumination, while the ZnO NPs as prepared and annealed in vacuum exhibits only the steady increase. This difference is due to the curing effect of the oxygen vacancies in oxygen condition. SEM images display no morphological change between particles, indicating the change in their internal structures. PL spectra shows the decrease of the deep - level peak when the ZnO NPs are annealed in oxygen at 400℃. At the annealing temperature of 600 ℃, PL spectra exhibits the different tendency of their behavior and it is assumedly due to the improved crystalline at the temperature.

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