Improved Luminescence Properties of Polycrystalline ZnO Annealed in Reduction Atmosphere

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ABSTRACT

The luminescence properties of polycrystalline ZnO annealed in reducing ambience (H_2/N_2) have been studied. An effective quenching of green luminescence with enhanced UV emission from polycrystalline ZnO is observed for the reduced ZnO. The variations of the UV and green luminescence band upon reduction treatment are investigated as a function of temperature in the range between 20 and 300 K. Upon annealing treatment in reducing ambience, the optical quality of polycrystalline ZnO is improved. The UV to green intensity ratio of sintered ZnO approaches close to zero (~0.05). However, this ratio reaches more than 13 at room temperature for polycrystalline ZnO annealed at 800°C in reducing ambience. Furthermore, the full width at half maximum (FWHM) of the UV band of polycrystalline ZnO is reduced compared to unannealed polycrystalline ZnO. Electron paramagnetic resonance (EPR) measurements clearly show that there is no direct correlation between the green luminescence and oxygen vacancy concentration for reduced polycrystalline ZnO.

Key words : ZnO, Optical Materials/Properties, Electron spin resonance

1. Introduction

Zinc oxide (ZnO) is a II-VI compound semiconductor with a direct band gap of 3.3 eV at room temperature. ZnO displays a wurtzite structure and exhibits extremely stable excitons as indicated by a binding energy of 60 meV, which is about three times larger than those of ZnSe and GaN. ZnO is also inexpensive compared to other compound semiconductors. Due to these properties, ZnO can be used for next-generation ultraviolet (UV) lasers and LEDs operating at room temperature. The polycrystalline ZnO exhibits a weak UV near band-edge emission and a strong defect-related deep-level emission peak near the green spectral region. Control of green luminescence, substantial increase of luminescence efficiency, and p-type doping are needed to fabricate LEDs and LDs. Various techniques are used to fabricate ZnO as single crystals, powders, and thin films, including sol-gel chemistry, spray pyrolysis, metal organic chemical-vapor deposition, DC and/or RF sputtering, thermal evaporation, spark processing, and thermal evaporation.[1-8] However, high optical quality ZnO is mainly obtained in the form of thin film via metal-organic chemical-vapor deposition (MOCVD)[3] and molecular beam epitaxy (MBE).[9,10]

Control of green luminescence with enhanced near band-edge emission is only reported for ZnO thin films prepared in reduction ambience.[11] In the present study, the preparation of high optical quality ZnO shows near band-edge UV emission devoid of deep-level green luminescence will be presented for sintered polycrystalline ZnO via simple forming gas reduction treatments. The influence of reduction treatments on the optical and structural properties of polycrystalline ZnO will be presented. The detailed luminescence behavior of annealed polycrystalline ZnO in reducing ambience, which is measured both at room temperature and low temperature (20 to 300 K) will also reported. Furthermore, the relationship between structural properties and luminescence as well as the origin of green luminescence from ZnO will be discussed briefly.

2. Experimental

Bulk ZnO samples were prepared by pressing ZnO powders (Aldrich Chem. 99.99% purity) into pellets 5 mm in diameter and 1 mm thick at 1000 psi. They were then sintered in air or pure O_2 (99.999 %) for 2 h at 1250°C (Hereafter, these samples will be designated as sintered ZnO). Post-annealing treatment of polycrystalline ZnO pellets (described as annealed ZnO) in flow of forming gas (H_2/N_2 = 5: 95) was performed in a tube furnace at various temperatures. The flow rate of the forming gas and the heating rate of the tube furnace during annealing were 5 sccm and 10 degrees per min, respectively. The samples were annealed at the desired temperature for 1 h, cooled down to room temperature, and pulled out for further analysis.

The PL equipment consists of a He-Cd laser with an output power of 30 mW, 50-mm collection optics, a 0.5-m scan-

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ning grating monochromator, and an air-cooled GaAs photomultiplier. The emitting light from the sample was focused into the entrance slit of the monochromator, which had a spectral grating of 1200 groves/mm, and then it was amplified by a PMT. A long-pass filter was inserted after the sample to block any scattered laser light. The cutoff wavelength of the filter at the UV side was about 340 nm. The sample was also placed in a vacuum chamber of a closed-cycle He refrigerator for temperature-dependent PL measurements between 20 and 300 K.

Raman spectra were measured at room temperature in a backscattering geometry with a microscope using a diode-pumped semiconductor laser with $\lambda = 532$ nm as an excitation source.

Electron paramagnetic resonance (EPR) analyses were obtained with 9.301587 GHz at liquid He temperature.

3. Results and Discussion

Fig. 1 shows the room temperature PL spectra of polycrystalline ZnO and annealed ZnO in reduction ambience. The sintered ZnO displays a typical PL spectrum, that is, small near band-edge UV emission with a large amount of green luminescence. It is quite interesting to note that for the ZnO samples reduced in forming gas at 400°C, the intensity of near band-edge UV emission initially increased with increasing green emission. The high energy shift of visible luminescence accompanied by a decrease of near band-edge UV emission was obtained for polycrystalline ZnO reduced at 600°C. The most startling finding is that the reduction in forming gas at 800°C exhibited improved UV luminescence with an annihilation of green luminescence. We have generally observed that reduction treatment of polycrystalline ZnO yields improved UV luminescence with effective quenching of green luminescence with reduction temperatures in the range between 600°C and 800°C. It is further
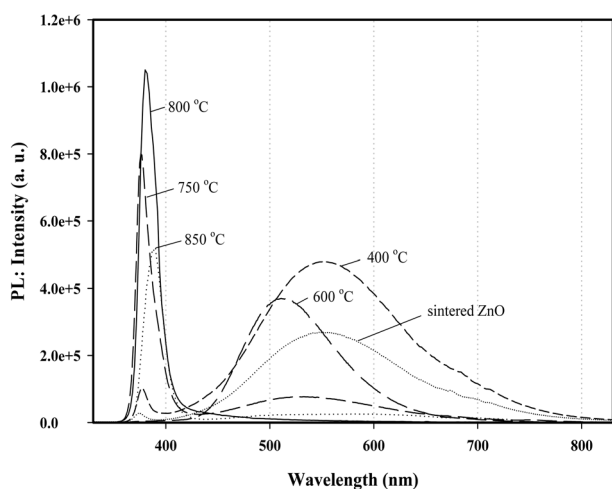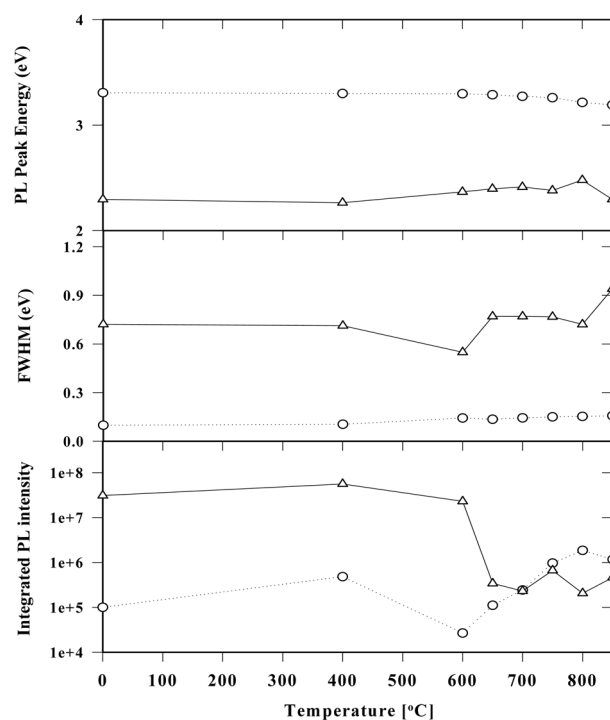
Fig. 2. Reduction-temperature dependence of PL peak energies, FWHM, and integrated intensity of polystalline ZnO annealed in forming gas. The open circles (○) and triangles (△) correspond to UV and green emission bands, respectively.

observed that reduction treatment at 850°C results in a red shift of UV luminescence along with reemergence of defect-related green luminescence.

The summarized dependence of PL peak energy, full width at half maximum (FWHM), and integrated PL intensity on the reducing temperatures is shown in Fig. 2. The PL peak energy of near band-edge UV emission shows a red shift upon reduction treatment. When the reduction temperature is set at 850°C, the polycrystalline ZnO exhibits a PL peak maximum position of 395 nm. In contrast, the green luminescence displays blue shift upon reduction. However, this blue shift is not gradual. The largest blue shift is detected when the reduction temperature is set at 800°C. Further the increase of reduction temperature to 850°C resulted in the decrease of PL peak energy of green luminescence. The FWHM of near band-edge UV emission increases with increasing reduction temperatures. Also, the FWHM of the green emission band increases with increasing reduction temperature. However, this increase is not monotonic, that is, the FWHM decreases at 600°C and 800°C. The PL intensity of green luminescence decreases with increasing reduction temperatures. The integrated PL intensity of near band-edge UV emission initially increases with reduction temperatures up to 400°C and then decreases at 600°C. Further increase of the reducing temperature results in increase of the PL intensity of UV band and shows max at 800°C. The emission in the UV region cor-
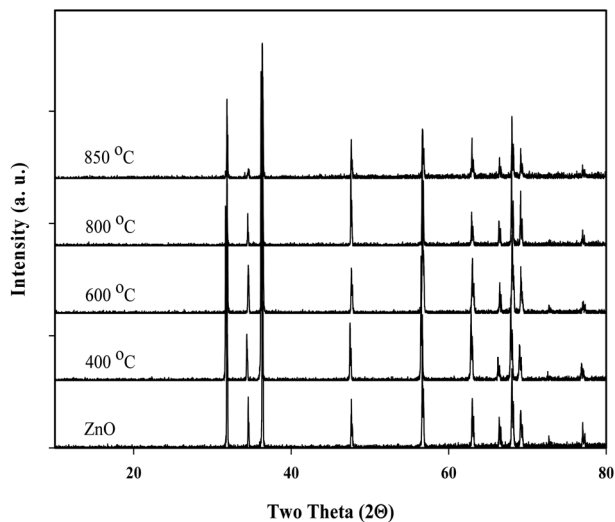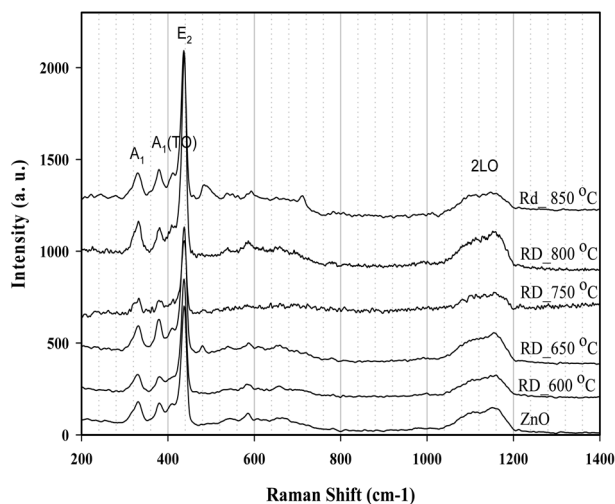

Fig. 1. Room-temperature photoluminescence spectra of sintered ZnO and annealed ZnO in reducing ambience. The reduction temperatures are indicated.

Fig. 3. X-ray diffraction of sintered ZnO and annealed ZnO in reducing ambience. The reduction temperatures are indicated.


Fig. 4. Room-temperature Raman spectra of sintered ZnO and annealed ZnO in reducing ambience. The annealing temperatures are indicated in the figure.

responds to the recombination between electrons in the conduction band and holes in the valence band.[12] The visible green emission is generally associated with intrinsic defects in ZnO.

The crystal structures of polycrystalline sintered ZnO and reduced ZnO were characterized by a conventional wide-angle X-ray diffractometer, and the results are shown in Fig. 3. All the diffraction peaks of the sintered ZnO and reduced ZnO confirm their polycrystalline nature. There are no other diffraction peaks associated with ZnO for reduction treated ZnO.
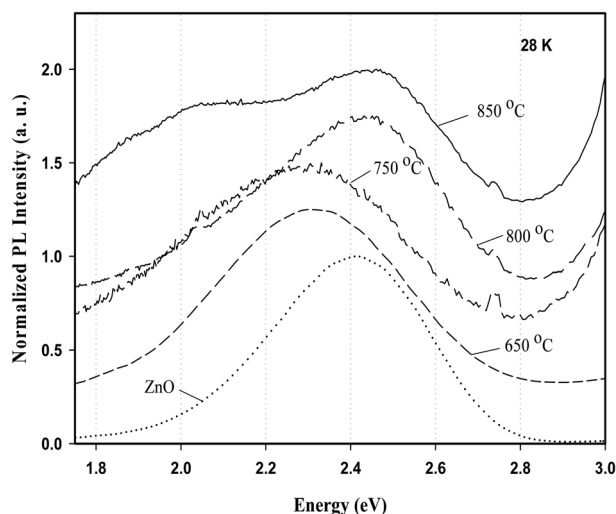
The Raman spectra of sintered ZnO and reduced ZnO in forming gas at room temperature are shown in Fig. 4. Bulk ZnO exhibits a strong peak at 438 cm^{-1} and pronounced peaks at 331 and 380 cm^{-1}, which correspond to E_2, A_1, and
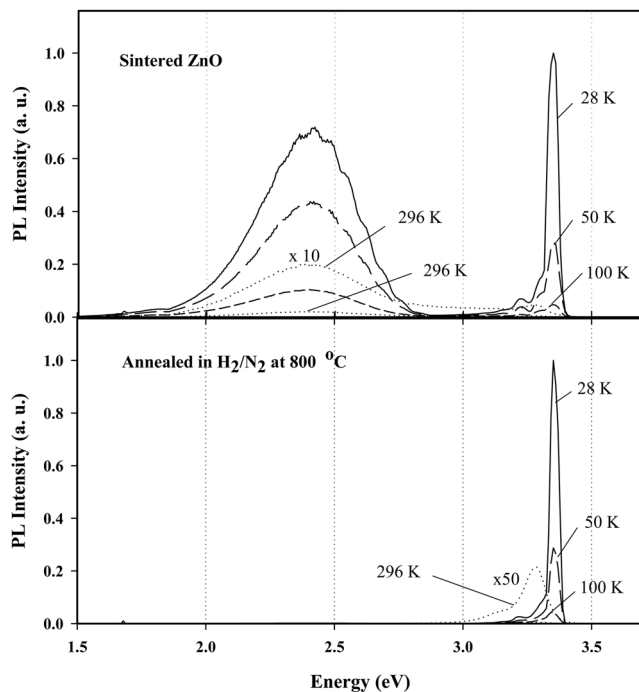
Fig. 5. Low-temperature photoluminescence spectra of sintered ZnO and annealed ZnO in reducing ambience at 800°C. Measurement temperatures are indicated.

A_1 symmetry with the transverse optical mode, respectively. A broad band from 520 to 700 cm^{-1} with peaks at 540 and 584 cm^{-1} and weak peaks at 657 cm^{-1} is also detected. These peaks agree well with the reported Raman spectra of ZnO powder.[13] The Raman spectra of reduced ZnO in H_2/N_2 at various temperatures are quite similar to those of bulk ZnO. The Raman results also clearly demonstrate that all the vibrational modes are associated with ZnO and are in good agreement with the XRD results. The vibrational mode at 580 cm^{-1} is thought to be related to defects, such as the formation of oxygen deficiencies, interstitial Zn, and free carrier.[14] Interestingly enough, the intensity of 580 cm^{-1}, which is attributed to intrinsic defects in ZnO, generally tends to decrease with increasing reduction temperatures up to 750°C, and further annealing in reduction treatment shows the re-emergence of this vibrational mode. However, there are some discrepancies between this Raman vibrational mode at 580 cm^{-1} and the luminescence behavior of reduced ZnO. Specifically, we could detect the largest effective quenching of green luminescence at 800°C, namely, the smallest intrinsic defect of polycrystalline ZnO.

The low-temperature PL spectra of sintered ZnO and annealed ZnO in reducing atmosphere at 800°C are shown in Fig. 5. The measurement temperatures are indicated. Sintered ZnO displays a strong PL emission peak at 3.349 eV along with peaks at 3.288 and 3.223 eV. The peak at 3.349 eV conforms to donor-bound exciton,[15] and the peaks at 3.288 and 3.223 eV correspond to donor-acceptor pairs.[16] No PL peak shift is detected for the green lumines-

Fig. 6. Normalized photoluminescence spectra of sintered ZnO and annealed ZnO in reducing ambience measured at 28 K. The annealed temperatures are shown in figure. The deep-level defect regions are only displayed.

Fig. 7. The integrated intensity ratios of UV-to-green of sintered ZnO and reduced ZnO as a function of PL measurement temperatures.

cence of the sintered ZnO. The measured FWHM of these peaks are 48, 38, and 85 meV. The PL peaks of annealed ZnO in reducing ambience are slightly blue shifted to peaks at 3.356, 3.297, and 3.228 eV, respectively. The FWHMs of reduced ZnO are slightly decreased to 39, 34, and 67 meV, respectively. Furthermore, the green luminescence is effectively quenched for the reduced polycrystalline ZnO. However, a careful observation of the PL spectra clearly reveals the existence of green luminescence with reduced intensities. The normalized PL spectra of the green spectral region, which are measured at 28 K, are shown in Fig. 6. There are some interesting findings worth mentioning for the reduced polycrystalline ZnO. Specifically, the PL peak position of the green luminescence band tends to display a low energy shift from 2.41 eV of sintered ZnO to 2.28 eV of annealed polycrystalline ZnO up to 750°C. Moreover, the FWHM of annealed ZnO in reducing ambience is increased. At an annealing temperature of 800°C, the green emission band reverted to 2.42 eV. Further increase of annealing temperature to 850°C yields two broad emission bands peaking at 2.10 and 2.45 eV. The evolution of the 2.1 eV emission band can be attributed to the various origins of intrinsic defects. However, the origin of 2.1 eV emission band and its assignment cannot be made at present.

The integrated intensity ratios of UV to green as a function of PL measurement temperatures are depicted in Fig. 7. The measured UV to green ratio of sintered ZnO is 0.04. High optical quality ZnO films grown by MBE display this value of 20 at room temperature due to the ultraclean environment and the high-purity source materials.[17] Interestingly enough, the UV to green ratio (I_{UV}/I_{Gr}) of the polycrystalline ZnO annealed in reduction ambience is about 13. Although the range of variation, that is, the UV to green ratio, is quite
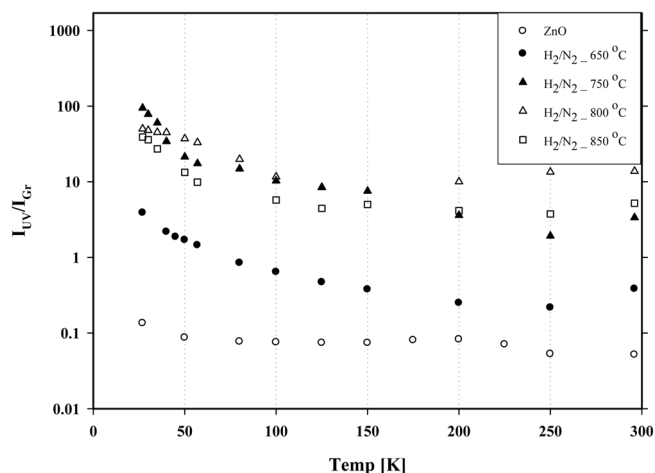
small, the intensity ratio (I_{UV}/I_{Gr}) tends to decrease with increasing temperatures for sintered ZnO. The decrease of I_{UV}/I_{Gr} was detected with increasing temperature along with a wider range of variation for the polycrystalline ZnO annealed in forming gas. The largest increase of the ratio was detected for ZnO annealed at 750°C at low temperature. However, the largest increase of ratio at room temperature was detected for the sample annealed at 800°C. These results clearly demonstrate that the reduction treatment of polycrystalline ZnO yields improved UV luminescence with effective quenching of green luminescence.

ZnO is a well known nonstoichiometric ceramic material. Various intrinsic defects, such as oxygen vancancy V_o, Zn vacancy V_{Zn}, Zn interstitial Zn_i, oxygen interstitial O_i, and antisite oxygen O_{Zn}, are known for ZnO. These defects are considered to be the origins of green luminescence from ZnO.[18-25] The concentrations of V_{Zn}, O_i, and O_{Zn} are proportional to that of $P_{O2}^{1/2}$ in annealing. However, the concentrations of Zn_i and V_o are proportional to that of $P_{O2}^{-1/2}$. Thus, in a reducing atmosphere, only the concentrations of Zn_i and V_o are affected greatly and increase with decreasing oxygen pressure. Therefore, to further study the relationship between oxygen vacancy and the intensity of green luminescence, electron paramagnetic resonance studies of sintered ZnO and ZnO samples annealed in H_2/N_2 ambience at selected temperatures were carried out, and results are given in Fig. 8. The resonance positions for the spectra correspond to a g-factor of about 1.96, which is associated with oxygen vacancy, and a g-factor of about 2.10. The detected g-factors agree well with the reported value.[19,26-29] It is expected that the oxygen vacancy concentration increases with increasing reduction temperature. Interestingly, the polycrystalline ZnO which was annealed at 400°C exhibited the largest amount of oxygen vacancy, judging from EPR results, and the largest defect related green luminescence, as seen in Fig. 1. A slightly reduced oxygen vacancy concen-
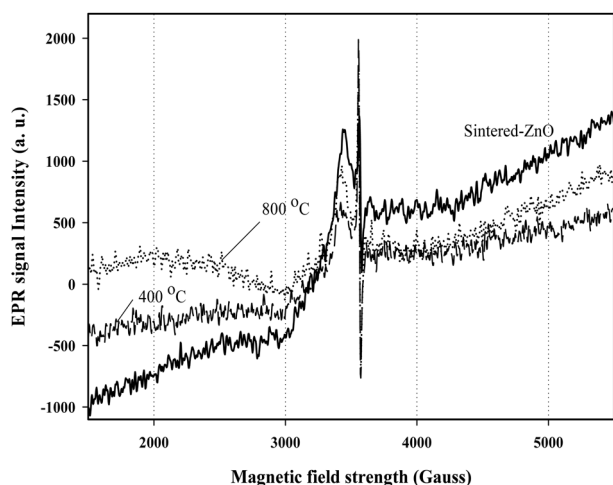
Fig. 8. Electron paramagnetic resonance spectra of polycrystalline ZnO and ZnO annealed in forming gas at 400°C and 800°C.

tration was detected for polycrystalline ZnO reduced at 800°C. However, it was possible to obtain ZnO devoid of defect-related green luminescence from polycrystalline ZnO reduced at 800°C as seen in Figs. 1 and 5. From these results, we are certain that V_o is associated somewhat with the green luminescence of polycrystalline ZnO, but it is not its sole origin. Interestingly enough, this result is quite contrary to the results reported by Vanheusden et al.,[19] and Ogata et al.,[30] but it is similar to the results reported by Fu et al.[25] The discrepancies among the results may be due to the different kinds and different numbers of defects, depending on the ZnO forms and preparation conditions used in the various studies.

The calculated energy levels of the intrinsic defects of ZnO films are reported, and the calculated energy levels of V_{Zn}, Zn_i, V_o, O_i, and O_{Zn} are 3.06, 2.9, 1.62, 2.28, and 2.38 eV, respectively.[25] It is interesting to note that the low-temperature PL studies of polycrystalline ZnO annealed in reducing ambience display PL peaks at 2.28 and 2.41 eV with greatly reduced PL intensities. It has also been reported that the PL peak of 389.2 nm (3.19 eV) was observed for ZnO with O_i.[31] We have observed a PL peak at 3.18 eV of polycrystalline ZnO annealed at 850°C. Therefore, O_i and O_{Zn} might be the cause of the green luminescence of reduced polycrystalline ZnO. At this point, the origin of green luminescence from polycrystalline ZnO seems to be more complex and does not solely stem from oxygen vacancy.

4. Conclusions

This paper reported the detailed luminescence properties of sintered ZnO and annealed ZnO in reducing temperature both at room temperature and at low temperatures. Their structural properties were investigated by XRD and Raman measurements. Sintered ZnO displayed a weak UV luminescence, which is related to near band-edge emission, with

pronounced broad green luminescence. The integrated UV-to-green ratio of sintered ZnO was close to zero. It is clearly evident that the annealing of polycrystalline ZnO in forming gas tremendously improves the UV intensity and effectively quenches green luminescence. That is, the UV-to-green ratio is increased to about 13. The origin of the green luminescence band from reduced polycrystalline ZnO is not associated with Zn_i and V_o, but it is probably related to O_i and/or O_{Zn}.

Acknowledgments

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