Luminescence of bound excitons in epitaxial ZnO thin films grown by plasma-assisted molecular beam epitaxy

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Luminescence properties of ZnO films, which have been epitaxially grown on *c*-sapphire (0001) substrates by plasma-assisted molecular beam epitaxy, are investigated by means of different excitation sources and their measurement conditions. With the increase of measurement temperature, photoluminescence spectra clearly present, the appearance of different bound-exciton peaks (I_{10} line) with an abrupt increase of emission intensity at the measurement temperature of 30-50 K. Hypothetical explanations on the basis of thermalization effects, vibronic/rotational resonance states, and the involvement of the B-valence level in emission are given. In cathodoluminescence (CL), the deep level emission intensity was enlarged with the electron beam penetration depth due to the higher defect density near the interface between ZnO and the sapphire. From the CL image of the ZnO film, the dislocation density was estimated as 6×10^8-$3\times10^9/\mathrm{cm}^2$. The lasing phenomenon was observed at the threshold power density of 1.3 $\mathrm{MW/cm}^2$ at 300 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2150602]

I. INTRODUCTION

Due to its wide band gap (3.37 eV), high exciton binding energy (60 meV) and optical gain ($300\ \mathrm{cm}^{-1}$),[1] and lower growth temperature than GaN, ZnO has been proposed as a next-generation optoelectronic material.[2] Various forms of ZnO such as polycrystalline thin films,[3] epitaxial thin films,[4,5] nanowires,[6] nanobelts,[7] and nanotubes[8] have been investigated depending on the aimed applications. Among them, epitaxial ZnO films have been noticed as a candidate material for ultraviolet (UV)/blue light emitting diode/laser diode (LED/LD) replacing III-V semiconductors. A better understanding of the luminescence properties of epitaxial ZnO thin films would be very crucial in designing and developing such devices.

In this article, photoluminescence (PL) and cathodoluminescence (CL) of epitaxial ZnO films grown by plasma-assisted molecular beam epitaxy (PA-MBE) and their temperature dependence are reported and discussed on a collective basis in terms of bound-exciton formations. Temperature-dependent PL spectra show the abrupt disappearance and resonant emergence of different bound-exciton peaks around the temperature of 30–40 K. An obvious lasing phenomenon in CL spectra was observed and the dislocation density was calculated from the obtained CL image.

II. EXPERIMENT

High-quality undoped ZnO thin films were grown on a c-$\mathrm{Al_2O_3}$ (1000) single crystal by PA-MBE. Metal Zn grains (6N purity) were used as a Zn source and chemically active oxygen atoms were assisted by rf discharge at 450 W. A low-temperature homobuffer ZnO layer of 15 nm was deposited at 500 °C prior to the growth of thick ZnO at a high temperature and then annealed in an O plasma environment at 680-800 °C. By the observation of a RHEED pattern, the layer by layer growth mode (two dimensional) was well kept up to 760 °C, but it changed into a Stranski–Krasnov mode (three dimensional) at 800 °C. Other experimental procedures were well described in detail elsewhere.[9] For the observation of the exciton behavior, photoluminescence (PL) spectra was taken on as as-deposited ZnO films in the temperature 10-300 K. As an excitation source, the He-Cd laser ($\lambda=325$ nm) was used and the incident angle and power was fixed at 45°. In parallel, cathodoluminescence (CL) was also obtained at 80 K and 300 K using field-emission scanning electron microscopy (FE-SEM) for investigating the dependence of the electron beam power density and for the estimation of the dislocation density.

III. RESULTS AND DISCUSSION

A. Photoluminescence

In the previous study, the ZnO thin film grown on a thin low-temperature ZnO buffer layer of 15 nm at 760 °C showed very high-quality crystalline and electrical properties, as evident from the full width at half-maximum (FWHM) of the ω-rocking curve over ZnO (0002) was 86 arcsec, and its mobility was almost equal to $\mu=105\ \mathrm{cm}^2/\mathrm{V\ s}$.[9]

Figure 1 shows PL spectra of ZnO, grown at 760 °C, taken at various temperatures from 10-300 K. Below 30 K,

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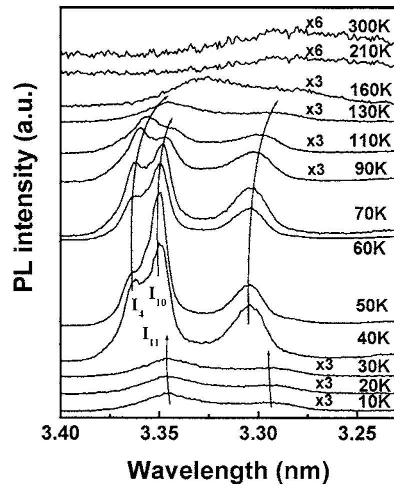

FIG. 1. Photoluminescence spectra of undoped ZnO thin film at temperatures 10-300 K grown on LT-ZnO/Al_2O_3(1000) at 760 °C.

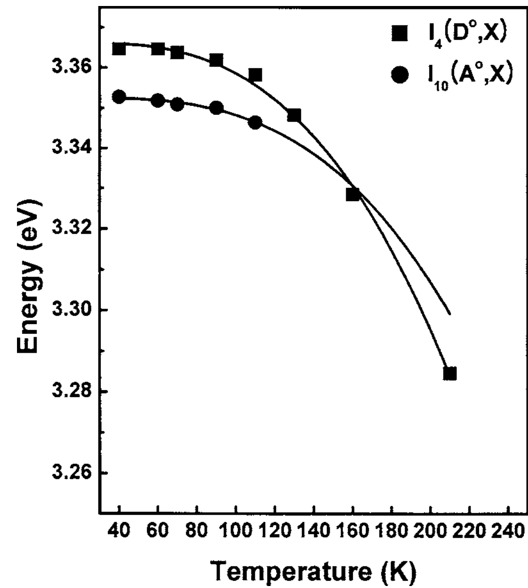

FIG. 2. Temperature dependence of the emission energies of a ZnO thin film for neutral donor bound emission I_4 (■) and for neutral acceptor bound exciton I_{10} (●). The solid lines denote the calculation using modified Varshni's formula.

an emission is observed at 3.3485 eV that can be attributed to the bound exciton recombination, I_{11}, as reported through magnetophotoluminescence experiments.[10,11] Two peaks in the lower-energy side, at 3.2958 eV and 3.223 eV are clearly observed and show the energy separation of about ΔE =72.8 meV (not shown here), which is consistent with the previous observation of the energy of an LO phonon.[12] Therefore, they can be easily conjectured to relate with optical phonon replicas of a bound exciton, BE_x-mLO (I_2 =3.3678 eV), which has been commonly assigned to ionized donor bound excitons.

As the temperature increases, I_{11} disappears at higher temperatures above 30 K. Instead, a new peak is clearly observed around 3.352 eV at 40 K and shows the maximum intensity at 50 K. Since the photon energy of this luminescence is slightly higher than I_{11}, and is very close to the 3.3531 eV line from Ref. 11, it can be temporarily assigned as another bound exciton, I_{10}. The chemical nature of these two bound exciton emissions I_{10} and I_{11} still remains to be undetermined. At the lower photon energy side, two more peaks are also found at 3.3075 eV and 3.235 eV (ΔE =72.5 meV) for $T>40$ K and are designated as optical phonon replicas of a free exciton, E_x-mLO (A_L=3.3795 eV). This result indicates that optical phonon replicas related to bound exciton behave differently with the increase in temperature. All the BE_x-mLO lines, which exist until 30 K, were disappeared at 40 K and the new E_x-mLO lines appeared above 40 K. These results are in agreement with the previous results of LT PL measurements on a ZnO single crystal, grown by the vapor transport method, where the BE_x-mLO lines were present at the temperature higher than about 50 K.[12] The complete disappearance of the BE_x-mLO was explained by the fact that this temperature, 50 K (k_BT =4.3 meV, k_B: Boltzmann constant) was comparable with the binding energy of the excitons to the impurities lowered by an attraction via the van der Waals interaction between them. This cease of phonon side bands above 30 K indicates that this phonon is explicitly interacted with any of the bound excitons, $[I_0(3.3725), I_1(3.3718), I_{1a}(3.3679), I_2(3.3674)]$ as the deduced bound exciton emission energy from BE_x-mLO is about 3.372, (3.368) eV. The localization energy of this line I_0 was reported as much as 3.4 meV (I_1 =4.1 meV, I_{1a}=8.0 meV, I_2=8.5 meV),[11] which corresponds to the intermediate thermal energy of 30 K (=2.58 meV) and 40 K (3.5 meV). It can be easily suggested that this bound exciton is certainly excited with the increase of temperature and consequently the interaction between free charges and phonons is enhanced. This conjecture is well sustained by the observation of phonon subband related to the free exciton above 30 K.

Figure 2 shows the peak positions of the observed excitonic emission lines against temperature. Assuming that the peak positions of the donor bound exciton, I_4 and acceptor bound exciton emission, I_{10} vary with the temperature as the energy band gap, the dependence of the peak position on temperature is better fitted to the modified Varshni's model[13] like Eq. (1) rather than a conventional one for semiconductors,

$$E_x(T) = E_x(0) - \alpha T^4/(T+\beta)^3, \quad (1)$$

where α, β, and $E_x(0)$ are fitting parameters. This function fits the data much better than any other expression used for ZnS.[14–16] The temperature dependence of the exciton energy typically shows two different asymptotic behaviors. At very low temperatures, the trend is proportional to T^4 due to electron–phonon scattering, while for temperature higher than 80 K it becomes linear due to lattice thermal expansion.[17] As shown in Fig. 2, $E_x(0)$ is 3.3662 eV and 3.3526 eV for donor bound emission and acceptor bound emission and the obtained α is about 1×10^{-2} eV/K and β is 405 and 555 eV/K, respectively. The β value is expected to be correlated with Debye temperature θ_D and the reported values for ZnO bulk and powder were 416 K and 477±65 K, respectively. Therefore, the obtained values of β above are

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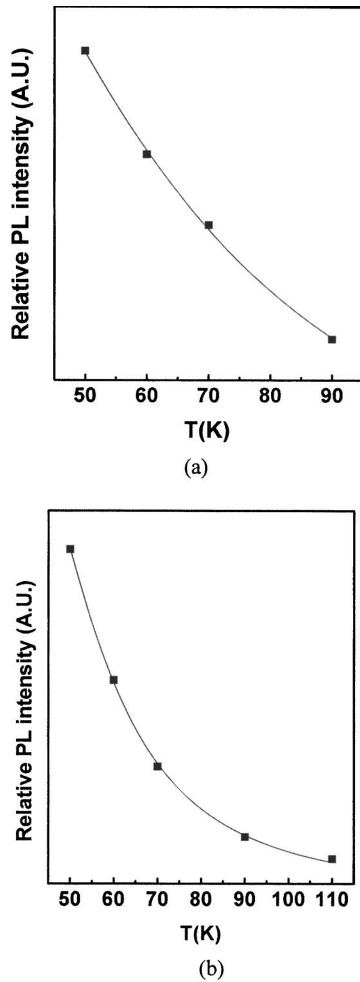

FIG. 3. Temperature dependence of the emission intensity of (a) neutral donor bound emission I_4 and (b) neutral bound acceptor emission I_{10}.

believed to be in reasonable agreement with θ_D=416 K within the error.

Figure 3 illustrates the energy dispersion of PL lines with the variation of temperature. The temperature dependence of the PL intensity can be expressed by Eq. (1),[18] where C_1 is the fitting parameter and ε_1 is the activation energy,

$$I = I_0/[1 + C_1 \exp(-\varepsilon_1/kT)], \tag{2}$$

where luminescence intensity, I, is defined as the area of an emission band and calculated by the Lorentzian distribution. By fitting the Arrhenius plot of the exciton emission intensity, which corresponds to the energy for thermal release of excitons from the neutral donors (acceptors), $[D^0(A^0),X] \rightarrow D^0(A^0)+X$, the activation energies for the subpeaks at 368.5 nm (=3.3645 eV) and 369.9 nm (=3.3518 eV) at 40 K are estimated as 13.3 meV and 23.1 meV, respectively. The E_a=13.3 meV differs from the reported values of 8.4 meV (I_2) and 9.5 meV (I_3) and 9.9 meV (I_{3a}),[8] but is rather close to E_a=13.0 meV for I_4. Hence, the 368.5 nm (3.3649 eV) peak can be assigned to the exciton bound donor, I_4 (D^0,X). Look *et al.* assigned the PL peak observed at 3.3631 eV to I_4 line and related this to the Zn_i, a shallow donor created after electron irradiation. Recently Meyer *et al.*[10] found that a shallow donor in the as-grown ZnO single crystal, which controls the conductivity, has a bound exciton recombination at 3.3628 eV, I_4. They attributed this particular donor to H by the correlation with magnetic resonance experiments. The E_a=23.1 meV of 369.9 nm (3.3527 eV) peak is very similar to 23.0 meV or 22.8 meV of I_{10}, corresponding to an exciton bound to neutral acceptor[10] or neutral donor,[11] however, the origin of this peak has not been exactly revealed yet.

Besides, the complete disappearance of I_{11} line at the temperature of 40 K, it is worthwhile to note that the luminescence intensity of I_{10} greatly increased and has the maximum value at 50 K. This feature can be ascribed to the following two processes. First we can think about the thermal effect. As the localization energy of the bound exciton line, I_{11} is 27.5 meV,[11] it can be presumed that the bound exciton of I_{11} is thermally excited to as much as 4.3 meV (=50 K) by thermalization effect, and this is very close to the energy difference of 4.7 meV between I_{10} and I_{11} lines.

Second, the energy level of the excitation resonance states of two exciton lines should be compared. Goutowski *et al.*[19] reported that the excited states of bound excitons were composed of mainly three different groups with respect to their position from the main luminescence line. The group I resonances were treated with regard to possible vibronic or rotational excited states, 1-3 meV above the main recombination lines. The group II resonances around 5 meV above the main lines were explained in terms of acceptor-exciton complexes involving one hole from the B valence band corresponding to the second lower Γ_7 band among three splitted valence bands: one Γ_9 and two Γ_7's, by spin–orbit interaction. The resonances of group III were shown to belong to excited electronic states of the (A^0,X_A) systems. For example, in the excitation spectra of the luminescence line, I_{6a} for polarization perpendicular to the crystal c axis $(E \perp c)$, group I lying 0.6-1.8 meV, group II between 4.3 and 6.5 meV, and group III locating 8.1-14.9 meV were found on the high-energy side of I_{6a}, respectively.[19] These groups of excitation resonances also occurred in the excitation spectra of all other luminescence lines of I_5 to I_{11}. It is plausible that the disappearance of I_{11} and the emergence of I_{10} around 40 K stem from the excitation to the vibronic/rotational resonance states or involvement of the B-valence level, considering the range of the obtainable thermal activation energy ($k_BT \sim 2.58$-4.30 meV) in the temperature range of 30–50 K.

B. Cathodoluminescence

Figure 4 shows the cathodoluminescence spectra for the ZnO thin films taken at 80 K (a) and 300 K (b). The peak position of near-band edge emission (NBE) in CL, taken at 80 K, is 368 nm (=3.3691 eV) and that increases to 376.9 nm (=3.2895 eV) at 300 K. From the inlet in Fig. 4(a), the energy difference between the second peak at 3.32 eV and the third peak at 3.25 eV is approximately 70 meV, and thus these two peaks are the replica of the free exciton $FX_B^{n=1}$ of a B-valance band involved.[20] When the peak intensity is normalized to that of NBE, the relative ratio of I_{rel} (=I_{NBE}/I_{DL}) of deep level (DL) emission centered around 550 nm is about 17 and the FWHM of the NBE peak taken at

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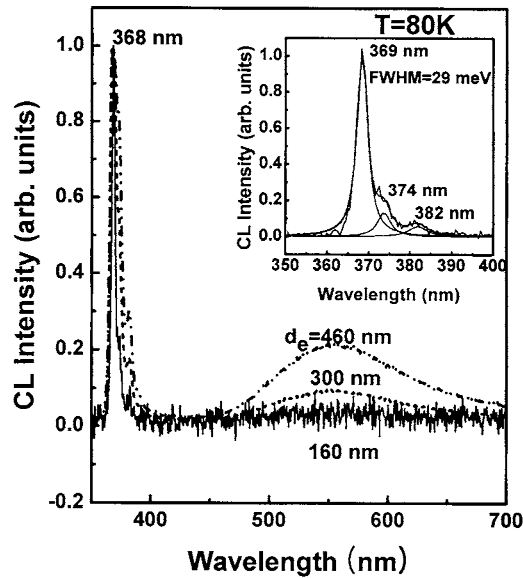


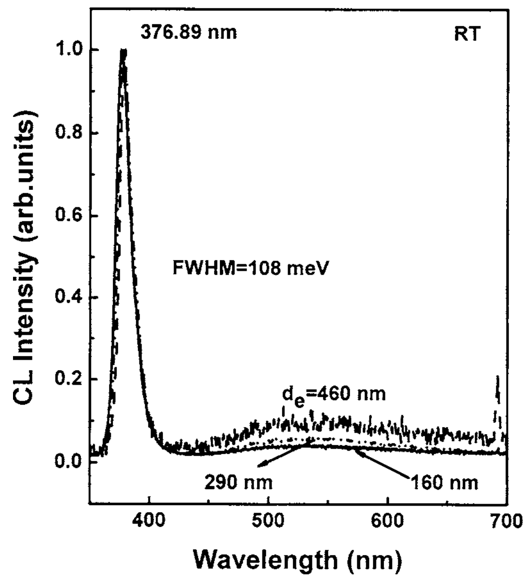
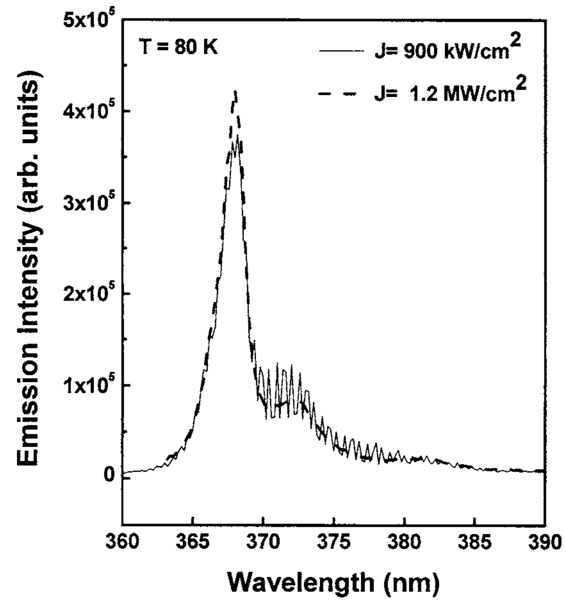


FIG. 4. Cathodoluminescence spectra of a ZnO thin film taken at (a) 80 K and (b) 300 K with the change of electron beam penetration depths.



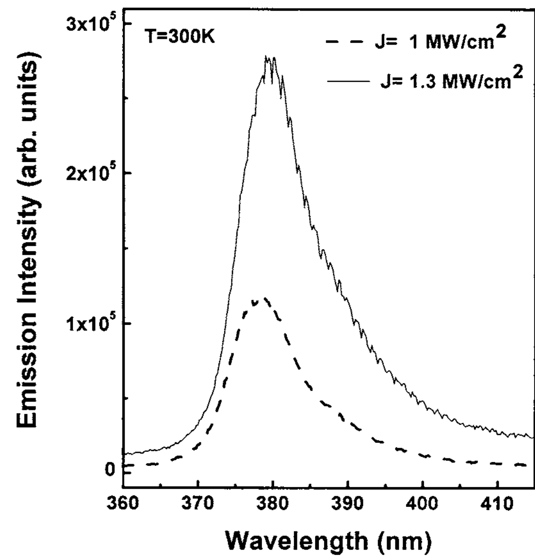


FIG. 5. Dependence of cathodoluminescence spectra on electron beam power density (J) of a ZnO thin film taken at (a) 80 K and (b) 300 K.

300 K is about 108 meV compatible with those of the ZnO film grown on sapphire (117 meV) (Ref. 21) and on GaN/SiV (129 meV),[22] which indicates that the film is believed to be of high quality. Simultaneously, in order to investigate the CL properties of e-beam penetration depth (d_e) dependence, the energy of the electron beam is increased to penetrate as deep as 60-460 nm. In both cases, I_{rel} generally decreases to about 5 at 80 K and 10 at 300 K, respectively, due to an increase of I_{DL} around 550 nm. This indicates that the defects are largely increased as the depth is approached at the interface of ZnO and sapphire and the result is easily comprehensive because the structural defect would be more concentrated at the interface caused by a large lattice misfit of 18.6% between a Zn lattice of ZnO and O sublattice of Al_2O_3(0001).

In order to test the feasibility of ZnO films grown on sapphire with an LT ZnO buffer layer as photonic material, high-power excitation experiments have been performed. Figure 5 illustrates the dependence of CL spectra on electron beam excitation power density J (W/cm^2) of ZnO at 80 K and 300 K. In Fig. 5(a), the CL spectrum measured at 80 K with the power density of $J=900$ kW/cm^2 is different from that taken at $J=1.2$ MW/cm^2. The latter spectrum consists of small oscillatory ripples at wavelengths longer than the wavelength of the main NBE of 367.9 nm. This phenomenon is described as a lasing, and the threshold power J_{th} corresponds to 1.2 MW/cm^2. In a similar way, J_{th} at 300 K increases slightly to 1.3 MW/cm^2. These values are very close to those observed in the laser-assisted MBE-grown ZnO thin film, and also provides good evidence that the ZnO film grown in this study is of high optical quality.

Figure 6 shows a CL image of local area, and using this the dislocation density of the ZnO film can be approximately

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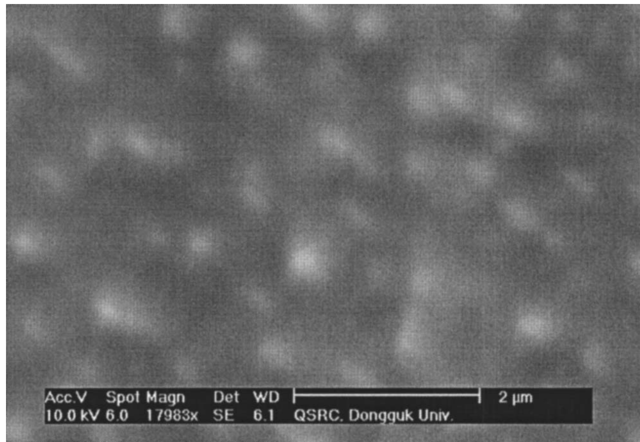

FIG. 6. Cathodoluminescence image of a ZnO thin film taken at the e-beam acceleration of 10 kV.

estimated. In general, the change of the CL intensity in the vicinity of the defects has been widely used to identify and map the spatial distribution of luminescent defects.[23,24] In Fig. 6, a large change in the brightness of the CL images is clearly observed near defects mainly related to dislocations. By counting the bright spots, the dislocation density of the ZnO grown LT, $ZnO/Al_2O_3(1000)$ is estimated about 6×10^8-$3\times10^9/cm^2$, which is less than the usual concentration of dislocations found in ZnO/Al_2O_3 about $10^{10}/cm^2$ for many epitaxial ZnO layers having mobility of less than $100\ cm^2/V\ s$.[25]

IV. CONCLUSIONS

Based on epitaxially grown undoped ZnO thin film on LT-buffered $ZnO/Al_2O_3(1000)$, photoluminescence and cathodoluminescence of bound excitons are investigated. As temperature increases, exciton bound to neutral acceptor, I_{11} was observed up to 30 K, but it disappeared at 40 K and then exciton bound to neutral donor I_4 and acceptor bound exciton I_{10} are observed. The disappearance of I_{11} and the occurrence of I_{10} were explained in terms of both the thermalization effect and the excitation to vibronic/rotational resonance states or involvement of B-valence level. In CL, the deep level emission was increased with the increment of the electron beam penetration depth due to the increase of the defect concentration at the interface of ZnO and sapphire. From the CL image of the ZnO thin film, the dislocation density was estimated as 6×10^8-$3\times10^9/cm^2$. As the power of electron beam, the lasing phenomenon was observed at the threshold power density $J_{th}=1.3\ MW/cm^2$ at 300 K.

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