Nonlinear paraexciton kinetics in a potential trap in Cu_2O under two-photon resonance excitation

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The nonlinear kinetics of paraexcitons confined in a harmonic trap in Cu_2O is examined by analyzing emission spectra under two-photon excitation of orthoexcitons as a function of the excitation power density. Strong saturation has been observed in paraexciton density without saturation of orthoexciton density. This indicates the occurrence of two-body collision that works as evaporative cooling process in the trap. We also show evidence for the direct creation of cold paraexcitons by a two-photon resonance excitation.

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I. INTRODUCTION

The exciton, or bound electron-hole pair, in the semiconductor Cu_2O has long been considered as a promising candidate for realizing excitonic Bose-Einstein condensation, due to large (150 meV) binding energy, no formation of an electron-hole droplet or exciton molecule, and the long lifetime derived from the forbidden band gap.[1] However, one serious factor that prevents the system from undergoing a phase transition is the decrease of density due to diffusion of the excitons. To overcome this difficulty, a scheme of three-dimensional confinement of the excitons can be introduced. It is realized by using a potential trap produced by inhomogeneous strain.[2,3]

More accurately, an electron-hole exchange interaction splits the $n=1$ exciton state into the spin-singlet orthoexciton and the spin-triplet paraexciton, with the paraexciton lying lower in energy. The orthoexcitons recombine in a nanosecond time scale by a quadrupole transition, whereas paraexcitons have a lifetime as long as submicroseconds to tens of microseconds[4,5] because their direct recombination is forbidden to all orders.

Recently, we have succeeded in loading a potential trap with paraexcitons using downconversion of orthoexcitons generated by two-photon resonance excitation.[5] One advantage of this method is the capability of injecting excitons at any location in the trap. This selective character enables precise observation of the exciton kinetics in the trap in spatial and spectral domains. Second, the stress in the trap makes the direct recombination of paraexcitons weakly allowed to provide information on the exciton kinetics through the emission spectrum. Theoretically, it is also possible to directly excite paraexcitons under stress by two-photon resonance,[6] which had never been verified experimentally though. If this new excitation method is demonstrated, the directly created paraexcitons should be more suited to the study toward Bose condensation than the orthoexciton-paraexciton system generated via downconversion of the orthoexcitons.

In this paper, we report saturation of paraexciton density versus excitation power density, which suggests new kinetic behavior of the paraexcitons in a trap, i.e., the possibility of their evaporative cooling. Additionally we show a demonstration of the two-photon resonance excitation of paraexcitons in the trap.

II. EXPERIMENT

A harmonic potential trap was produced by inhomogeneous stress applied to the Cu_2O crystal, as we published elsewhere.[5] The magnitude of the stress at the trap bottom was 2.6 or 2.8 kbar. The stress axis was chosen to be along [110] crystal axis, so as to maximize the paraexciton recombination rate. An infrared beam of 12 ns duration from a LiF: color center laser (Solar, CF150) was directed to one side (110) face of the sample to resonantly excite orthoexcitons or paraexcitons in the trap. The emission was observed by a charge-coupled device (CCD) camera (Wright Instruments, or Andor DU420) through a monochromator (Jobin Yvon THR1500, or Jasco CT25T) from the other (110) face. All the spectra were taken in time-integrated regime.

III. RESULTS AND DISCUSSION

Displayed in Fig. 1 are emission spectra of the excitons created at a rim of the trap with various excitation power densities with bath temperature of 2 K. The energy corresponding to the trap bottom for the paraexcitons is indicated by ω^p_{bott}. The energy for the orthoexciton trap bottom locates out of this spectral range at $\omega^o_{bott}=2.028$ eV. The two-photon excitation energy was fixed at $\omega^o_{pump}=2.031$ eV, about 2.7 meV (31 K) above ω^o_{bott}. The orthoexcitons are created at $K\sim 0$ in momentum space and spatially at a rim of the trap, as schematically shown by the inset. They recombine with and without assistance of phonons having almost flat dispersion (see the right inset). Here we focus on the latter or phonon-assisted emission, which reflects the exciton distribution in the momentum space. The sharp peak at $\omega^{o'}_{pump}=\omega^o_{pump}-\omega_{phonon}$ in the spectrum corresponds to the phonon-assisted emission of orthoexcitons of $K\sim 0$ at the

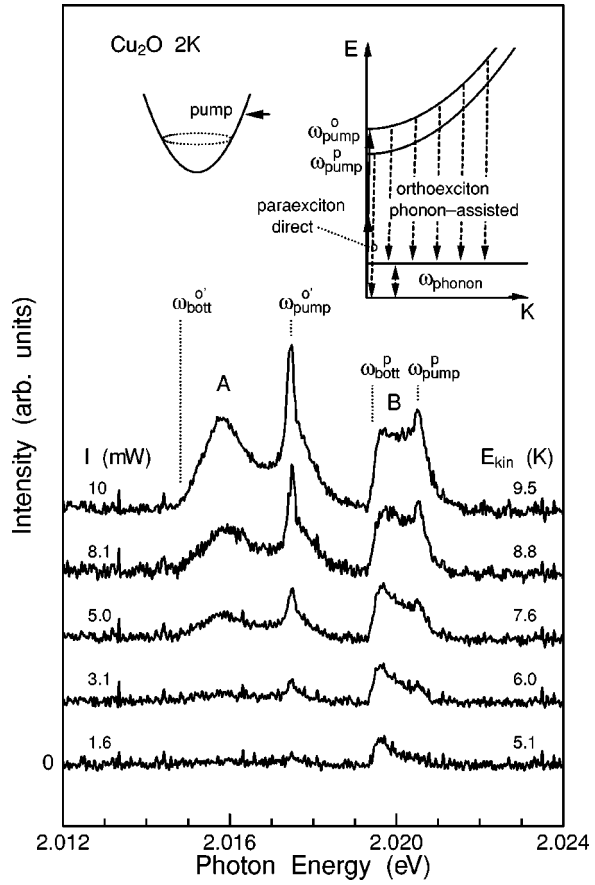

FIG. 1. Spectra of orthoexciton phonon-assisted emission and paraexcitons direct emission at 2 K with various excitation densities. Orthoexcitons are created at a rim of the trap with maximum stress of 2.6 kbar, by two-photon resonance excitation. ω_{bott} and ω_{pump} denote the exciton energies at the trap bottom and the pump spot, respectively. $\omega^{o'}=\omega^{o}-\omega_{phonon}$ corresponds to the edge of the phonon-assisted band of the orthoexcitons. Left inset: schematic illustration of a harmonic potential trap. Right inset: momentum-energy diagram for exciton recombination process at the pump spot.

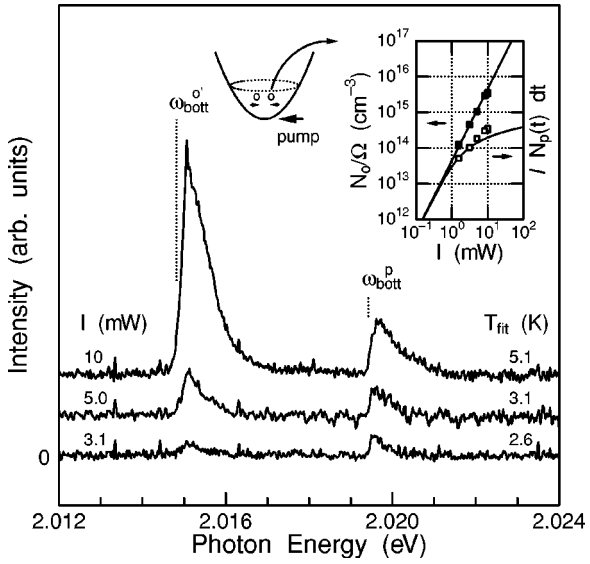

FIG. 2. Emission spectra under two-photon resonance excitation of orthoexcitons at the trap bottom. Inset: emission intensity vs excitation density. Solid squares for orthoexcitons and open squares for paraexcitons. The solid curves show results of calculation explained in the text.

pump spot, where $\omega_{phonon}=13.6$ meV is the phonon energy. The high-energy tail is due to orthoexcitons at the same location but those thermally populating in momentum space. The peak at ω^{p}_{pump} indicates paraexcitons formed by down-conversion of the orthoexcitons at the pump spot. This emission line is due to direct (i.e., no phonon-assisted) recombination of paraexcitons, which becomes allowed under stress in the trap. This process collects $K\sim 0$ paraexcitons only, but reflects the excitonic temperature when the excitons are confined in a trap,[2] as will be seen below.

Both orthoexcitons and paraexcitons are driven toward lower potential regions by motive force caused by the potential gradient.[3] This appears as broad features marked by A and B below $\omega^{o'}_{pump}$ and ω^{p}_{pump}, respectively. The low-energy edge of B agrees with the paraexciton energy at the trap bottom, ω^{p}_{bott}, whereas the peak of A occurs relatively higher above $\omega^{o'}_{bott}=\omega^{o}_{bott}-\omega_{phonon}$. This means that paraexcitons reach to the trap bottom while orthoexcitons of the short lifetime decay on the way. Another important point to note is that there is no upconversion of paraexcitons to orthoexcitons at the trap bottom, because no signal is observed at $\omega^{o'}_{bott}$.

Interestingly, clear difference is seen in the spectral shape of the paraexciton recombination line under different excitation densities. This suggests that paraexcitons distribute in the trap in a different way depending on the excitation power density. As the system is not in complete thermal equilibrium in any case, we cannot define the excitonic temperature. Instead, the mean kinetic energy of the exciton system, $E_{kin}=\int dEI(E)E/\int dEI(E)$ can be a measure of the degree of thermalization, where E is the energy measured from the potential bottom and $I(E)$ is the observed spectral shape. We find that E_{kin} ranges from 5 to 10 K as indicated in the figure.

This result shows that the excitons cool down toward the lattice more efficiently in lower excitation density than in the higher one. Competing with this cooling process, however, heating occurs at high density presumably due to some interaction (e.g., collisions) between two excitons. This process can be, in principle, described by a Boltzmann equation[7] including exciton relaxation in real, momentum, and energy spaces, but we choose to examine the two-body process in a simpler situation by selectively creating excitons at the trap bottom.

Figure 2 shows spectra taken under resonance excitation at the trap bottom ($\omega^{o}_{pump}=\omega^{o}_{bott}$), with the excitation power density I changed as shown at the left. The spectral shape of the direct recombination line of paraexcitons is again I dependent, but no anomalous peak (such as that seen in Fig. 1) was observed at ω^{p}_{bott}. Therefore, the system is expected to be close to the thermal equilibrium in this case. In fact, the spectral shape fits to a Maxwell-Boltzmann distribution function (assuming thermal equilibrium) multiplied by the

density of state in a harmonic potential trap,[8] $V(r)=\alpha r^2$,

$$I(E)^{trap}_{direct}=\int dr\,\delta(E-\alpha r^2)e^{-E/k_BT} \propto \sqrt{E}e^{-E/k_BT}, \quad (1)$$

where α represents the force constant of the trap and is typically 20 meV/mm^2 for paraexcitons in our experiments. The fit to Eq. (1) gives the temperature T_{fit} attached to each spectrum. The higher the excitation density becomes, the higher the temperature rises. Nevertheless, the system is colder than the cases shown in Fig. 1, for which we obtained $E_{kin}\geqslant 5$ K.

Solid and open squares in the inset are spectrally integrated intensity of the orthoexciton and paraexciton signals, as a function of *I*. For paraexcitons, the temperature-dependent fraction of excitons occupying the $K\sim 0$ state relative to the total number ($\propto \int dE E^2 e^{-E/k_BT}$) has been corrected using $T=T_{fit}$. Therefore, the plotted values represent total number of excitons of respective species in the trap, in relative scales. The orthoexciton number N_o shows a quadratic dependence as is expected for the two-photon excitation process. On the other hand, the paraexciton number N_p is sublinear to *I*.

Similar saturation in paraexciton density has been well known in the one-photon excitation regime.[2] The coupled rate equations

$$\frac{\partial N_o}{\partial t}=G-\frac{N_o}{\tau_{op}}+\frac{aN_p^2}{2\Omega}, \quad (2)$$

$$\frac{\partial N_p}{\partial t}=\frac{N_o}{\tau_{op}}-\frac{N_p}{\tau_p}-\frac{aN_p^2}{\Omega} \quad (3)$$

account for this behavior, where *G* is the generation rate, Ω is the effective volume of the exciton cloud, and $\tau_{op}=3$ ns is the downconversion rate which dominates the orthoexciton decay at low temperatures.[9] The paraexciton lifetime τ_p has been measured as 0.3 μs in our trap.[5] The nonlinear terms of N_p stand for the *Auger* process in which two paraexcitons collide, one recombines liberating the band gap energy with the other being ionized and then rebinding into an orthoexciton.

However, situations here are quite different from those in one-photon regime in the following points: (i) no saturation in orthoexciton intensity is seen, (ii) no upconversion of paraexcitons into orthoexcitons occurs, and (iii) the excitation is not cw.[10]

In order to reproduce the observed phenomena (i) and (ii), we should remove the rebinding term $+aN_p^2/2\Omega$ in Eq. (2). Then considering the duration of the laser pulse, which is comparable to τ_{op} but much shorter than τ_p, we separately use the Eqs. (2) and (3) for different temporal ranges. Namely, we assume a steady-state condition for orthoexcitons during the laser pulse and have a transient equation for paraexcitons after the laser pulse. This leads to quadratic dependence of the orthoexciton number

$$N_o=G\tau_{op}=1.4\times 10^{13}\times\beta\times(I/10\ \text{mW})^2, \quad (4)$$

where β is the two-photon absorption efficiency, and

$$\frac{\partial N_p}{\partial t}=-\frac{N_p}{\tau_p}-\frac{a_{net}N_p^2}{\Omega} \quad (5)$$

for paraexcitons, where $a_{net}=(1-\eta/2)a=0.8\times 10^{-7}$ cm^3/s is the *net* Auger constant including paraexciton rebinding efficiency η.[11] The solution to Eq. (5) is obtained as

$$N_p(t)=\frac{N_p(0)e^{-t/\tau_p}}{1+(a_{net}/\Omega)N_p(0)\tau_p(1-e^{-t/\tau_p})}, \quad (6)$$

with initial paraexciton number $N_p(0)=N_o$ given by Eq. (4). Since we measured spectra in time-integrated regime, the time integration of $N_p(t)$, $(\Omega/a_{net})\ln[1+a_{net}N_p(0)\tau_p/\Omega]$ should be compared with the experimental data.

The solid curves in the inset are calculated results with $\Omega=3\times 10^{-6}$ cm^3 assuming no expansion of the exciton cloud at early times during which the two-body process is dominant.[12] The absorption was evaluated to be 0.1% ($\beta=10^{-3}$) over the well for an incidence power of 10 mW. The calculation reproduces the data quite successfully. Our rough estimate of the density, 5×10^{15}/cm^3, at early times is about 1/30 of the critical density for condensation at 2 K.

If one-half of the paraexcitons taking part in the two-body collision are all ionized, they should rebind into orthoexcitons with some probability by spin randomization. This is not the case of our observation (ii). Alternatively, there can be an elastic collision without ionization in which one paraexciton goes across the trapping wall of ~ 17 K with carrying away the kinetic energy from the other paraexciton cooled and left in the trap. The hot paraexcitons away from the trap cannot emit light due to the forbidden nature under zero stress and mimic the nonradiative Auger loss $-a_{net}N_p^2/\Omega$. This process certainly reduces the temperature of trapped excitons like the evaporative cooling process, but does not account for the density-dependent heating. If a very small fraction of colliding paraexcitons release band gap energies by their nonradiative recombination and if the energies are shed to the rest of paraexcitons, one decaying paraexciton can warm up a large number of paraexcitons to the rim of the trap, causing the density-dependent heating. Therefore, the system temperature is most likely to be determined by the competition between this heating and cooling by elastic collision without ionization.

The mechanism of the downconversion of the orthoexcitons to paraexcitons has not been fully clarified, but it seems that emission of acoustic phonons is involved in the process. Due to the energy-momentum conservation during the conversion process, the kinetic energy of paraexcitons becomes finite. On the other hand, if one could generate paraexcitons directly using the paraexciton resonance, the initial kinetic energy of the paraexcitons is close to zero. The difference in the kinetic energy may affect the two-body collision rate

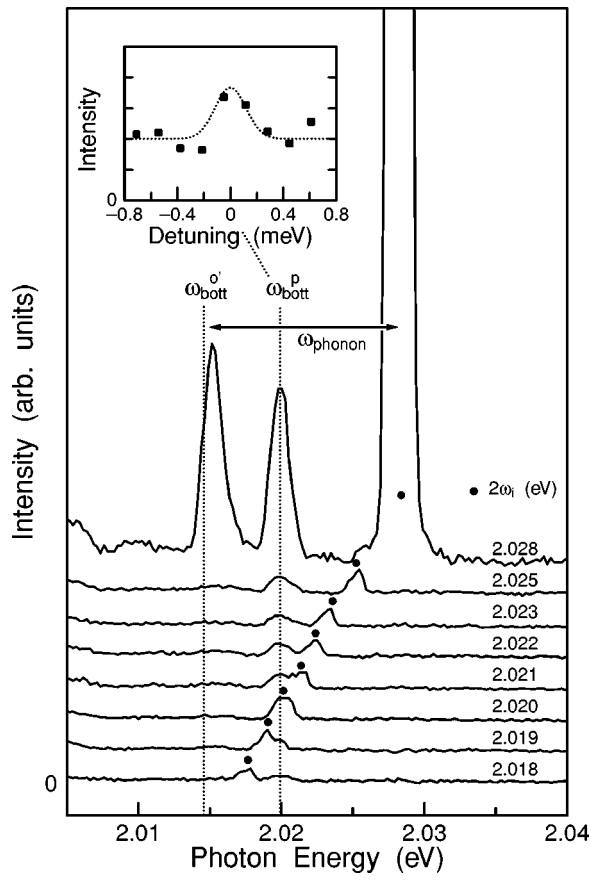

FIG. 3. Emission spectra of orthoexcitons and paraexcitons in a trap with maximum stress of 2.8 kbar. The two-photon excitation energy was changed from orthoexciton to paraexciton resonance. Inset: paraexciton emission intensity as a function of detuning from ω_{bott}^{p}. The dotted curve is to guide the eye only.

although the Auger process is to be independent of the exciton kinetic energy.[13] Furthermore, the selective creation of paraexcitons is appealing in view of the separation of the para-para collisions from ortho-para or ortho-ortho collisions, which is difficult in the exciton gas with a mixture of the different spin states and may provide new information on the paraexciton collisional interaction. In order to examine this possibility, we measured emission spectra with various two-photon excitation energies $2\omega_i$ ranging from orthoexciton resonance to paraexciton resonance. The spectral resolution was lowered so as to detect the weak signals.

Figure 3 shows emission spectra thus obtained. The strong peak at 2.028 eV under the resonance excitation of the orthoexcitons ($2\omega_i = 2.028$ eV) is the direct emission line of the orthoexcitons at the trap bottom. The phonon-assisted band also appears near $\omega_{bott}^{o'}$, showing the presence of the real orthoexcitons. Paraexcitons are generated through the downconversion of the orthoexcitons, and their direct emission line appears at ω_{bott}^{p}.

A striking feature was found under the excitation below the orthoexciton resonance ($2\omega_i \leqslant 2.025$ eV): the phonon-assisted band of the orthoexcitons was not observed whereas the paraexciton line appeared with considerable intensity. This means that no real orthoexcitons exist in the trap and that the exciton system consists of *only* paraexcitons. The two-photon resonance Raman scattering of paraexcitons is unlikely because it is a higher order process.

In addition to the paraexciton emission line, we observed more or less peak at $2\omega_i$ as marked by solid dots. The intensity of this peak for the excitation below the orthoexciton resonance is four orders of magnitude weaker than that for the orthoexciton resonance excitation. When the stress is removed, the paraexciton emission line disappears while this peak remains. From these facts, we attribute this peak to be off-resonant SHG scattering associated with the orthoexcitons.

Under the excitation close to the paraexciton resonance ($2\omega_i = 2.020$ eV), this scattering component overlaps the paraexciton emission line. The inset in Fig. 3 shows the intensity of the peak as a function of the two-photon excitation energy in this region. The base line is due to the scattering component at $2\omega_i$, which is not spectrally distinguished from the paraexciton luminescence near the resonance. We have found a slight resonance at ω_{bott}^{p}. The observed enhancement is about factor of 2.

We also measured the incident power dependence of the paraexciton emission intensity. It showed no saturation in our excitation range. This can be due to the quench of the two-body interaction at low density. Namely, because of the 1/10 paraexciton density of that in the orthoexciton resonance excitation, the two-body collision merely occurs and quadratic dependence is brought about, as seen in the inset of Fig. 2. Nevertheless, there still be a possibility that the two-body heating is suppressed under this novel excitation regime. For the production of a large number of paraexcitons by the two-photon resonance, another external perturbation such as a magnetic or electric field may be necessary to increase the two-photon transition probability.

IV. CONCLUSION

We examined nonlinear kinetics of paraexcitons in a trap by analyzing density-dependent emission spectra under two-photon excitation of orthoexcitons. When the orthoexcitons are created selectively at the trap bottom, the paraexciton temperature is lower than the case of injection at the rim. However, the temperature is raised under strong excitation. According to our interpretation, heating by the usual Auger process and evaporative cooling process (without ionization) compete in the trap. Furthermore, as a new excitation method of cold paraexcitons, we have observed two-photon resonance to paraexcitons.

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