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Growth of high-quality CuCl thin films by a technique involving electron-beam irradiation

Masayoshi Ichimiya [a,b,*], Le Quang Phuong [a], Masaaki Ashida [a], Tadashi Itoh [c]

[a] Department of Materials Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[b] Department of Physics, Osaka Dental University, Hirakata, Osaka 573-1121, Japan
[c] Institute for NanoScience Design, Osaka University, Toyonaka, Osaka 560-8531, Japan

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ABSTRACT

We have developed the molecular-beam epitaxy (MBE) method for CuCl thin films. The crystalline quality has been improved by an electron beam irradiation before the MBE growth. The qualified films show an exceptionally high speed nonlinear response of excitons at room temperature, wherein the excitons decay radiatively before its coherence is destroyed by dephasing. The radiative decay time of the excitonic state in films with a thickness of hundred nanometers reaches the order of 100 fs, which is much faster than the dephasing process. The shapes of the measured degenerate four-wave mixing spectrum and the radiative decay profile closely reflect those of the calculated induced-polarization spectrum and the radiative decay profile obtained by real-time analysis, respectively.

1. Introduction

The exciton resonance is essential for the achievement of an efficient nonlinear optical response. However, processes accompanied by the creation of excitons have been considered to be unsuitable for the optical gate devices in which the information carrying capacity is the most important, since the radiative lifetime of excitons is too long; it is in the order of hundred picoseconds or longer [1–4]. In nanocrystals, where the long wavelength approximation (LWA) is applied, the radiative decay rate of excitons increases with the system size due to the enhancement of wave coupling between light and excitons. In the LWA resume, light interact with nodeless-type ($n=1$) confined exciton and the enhancement is limited by the applicable range of the approximation, in which the spatial structure of light wave is neglected.

On the other hand, if the exciton coherences are extended to whole volume of the system in the size region over nanocrystals by improving the crystalline quality, wave functions of multinode-type ($n>1$) excitons can match with light wave with a wide range of the system despite the breakdown of LWA [5]. In such a regime, nonlinear optical response with an extremely high efficiency beyond the LWA regime is theoretically predicted [6]. In GaAs thin films, where the growth method of high-quality sample by molecular beam epitaxy (MBE) has been already established, observation of the degenerate four-wave mixing (DFWM) signal of $n=2$ exciton, which is forbidden in the LWA regime, is reported in Refs. [7,8], where the signal reaches 25 times larger than that in bulk crystal and the fast response times below 10 ps is observed [7,8]. If a new growth method for nanocrystals with high crystalline quality is established in a substance, where excitons are stable and strongly interacts with light more than GaAs, a high performance nonlinear optical device with ultrafast and high-efficient response may be realized.

I–VII semiconductor CuCl is a candidate for highly efficient optical devices in the near-ultraviolet region because of much stronger radiative coupling per unit cell volume [9] and huge exciton binding energy (about 200 meV). In the vicinity of room temperature, however, the nonlinear optical signal has never been observed because of the nonradiative process due to the interaction with the optical phonons is dominant. Thus, it has never been utilized except for the basic research at low temperatures. On the other hand, the exciton lifetime in CuCl is very short (below 1 ns [4]). Furthermore, the nonlocal theory predicted that a radiative width, which corresponds to an imaginary part of radiative correction due to long-range coherent coupling between light and multinode-type excitons, is several orders of magnitude larger than that in GaAs [10,11], and efficient nonlinear signal and ultrafast response beyond the case of GaAs is expected. In the present work, we have established a growth method of high-quality CuCl thin film to realize ultrahigh-speed response overcoming dephasing by optical phonons.

2. Experimental procedure

Our growth method of CuCl thin films were based on molecular beam epitaxy (MBE) [12]. CaF_2 (111) was used as a substrate.

* Corresponding author at: Department of Physics, Osaka Dental University, 8-1 Kuzuha-hanazono, Hirakata, Osaka 573-1121, Japan. Tel.: +81 7286 43061; fax: +81 7286 43161.
E-mail address: ichimiya@cc.osaka-dent.ac.jp (M.-n. Ichimiya).

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The lattice constant of CaF_2 is 0.5463 nm and the lattice mismatch with CuCl, which is derived with the lattice constant of CuCl (0.5406 nm), is 1.0%. Therefore, the heteroepitaxial growth of CuCl thin films is expected to be achieved on CaF_2 [13]. The substrates were derived from CaF_2 ingot by a cleavage in air, and the thicknesses were adjusted to be 1 mm to avoid to appear interference fringe on each optical spectrum. The cleaved substrates were set in a MBE chamber with the base pressure below 1×10^{-7} Pa and cleaned thermally in the ultra-high vacuum for 1 h at 650 °C before deposition. The substrate temperature was monitored by a thermocouple attached to the backside of the substrate holder during the deposition. A 40-nm-thick CaF_2 buffer layer was grown on the substrates kept at a temperature of 600 °C. The flux of CaF_2 was monitored by a quartz crystal oscillator, and the growth rate was 4 nm/min. The temperature of Knudsen cell of CaF_2 was kept around a temperature of 1120 °C during the growth of buffer layer. Before the growth of CuCl layer, a defocused electron beam generated from a typical reflection high energy electron diffraction (RHEED) system was irradiated onto the surface of CaF_2 buffer layer. Although the diameter of electron beam was controlled to a diameter of 4 mm, the irradiation area on the substrate was like a band with a width of 4 mm due to the very low glancing angle incidence of the electron beam. The accelerating voltage and beam current of electron beam were 5.0 kV and 10 μA, respectively. A CuCl layer was grown with the substrates temperature of 130 °C. The flux of CaF_2 was monitored by a quartz crystal oscillator, and the growth rate of CuCl was 2 nm/min. The temperature of Knudsen cell of CuCl was kept around a temperature of 200 °C during the growth.

In optical measurements, grown films were mounted in a helium flow cryostat and the temperature was controlled from 5 K to 300 K. DFWM was measured using the second harmonic of a mode-locked Ti:sapphire laser, whose repetition rate and pulse duration were 80 MHz and 110 fs, respectively. The photon energy of the pulse was tuned to approximately the transverse exciton energy of CuCl (3.2022 eV at 5 K) and the spectral width was approximately 20 meV, which covered the exciton resonance region. The light was split into two or three (transient grating configuration) pulses and all of them were focused onto the same spot on the sample surface. In the DFWM measurements, the polarizations of the two pulses were parallel and the delay time was set to be zero. In transient grating (TG) measurements, the polarization of the probe pulse was perpendicular to that of the parallel polarized pump pulses and the delay time between pump pulses was also set to be zero. The signal light was transmitted through an optical fiber to a monochromator equipped with a charge-coupled device (CCD). The spectral resolution was better than 0.08 meV. The film thickness at the measured spot was derived by fitting to the reflection spectrum measured using the same geometry and excitation light as those in the measurement of DFWM. The film thickness as well as the phase decay constant at the measured spot and the exciton energies at each temperature were derived by fitting to the reflection spectrum measured using the same geometry and excitation light as those in the measurement of DFWM.

3. Results and discussion

Fig. 1 shows a comparison of surface morphology in a CuCl thin film with a thickness of 42 nm whether the electron beam is irradiated or not. The atomic force microscope (AFM) image of an area where the electron beam was not irradiated is shown in Fig. 1(a). Although MBE has succeeded in growing high quality thin films for III–V and II–VI semiconductors, the prominent surface roughness like aggregated island structures is observed over the whole of the surface, and epitaxial growth of CuCl on CaF_2 (111) by this traditional MBE method is confirmed to be difficult. On the other hand, although the other growth conditions are the same between two kinds of areas, the roughness is not observed in the area where the electron beam was irradiated as shown in the AFM image of Fig. 1(b). This result shows that the surface morphology of CuCl thin films grown by MBE is extremely improved by the electron-beam irradiation. The growth mechanism can be explained as follows. Core electrons of fluoride ions at the surface of CaF_2 (111) are emitted by the electron beam, and neutral fluorine atoms or positive fluoride ions are removed from the surface. As a result, chloride ions occupy the fluorine vacancies at the beginning of MBE growth, and homoepitaxial-like growth of CuCl can be achieved. Similar improvement in the crystalline quality by the electron beam irradiation on CaF_2 (111) surface has been reported for thin films of GaAs and ZnO [14,15].

Fig. 2(a) shows the DFWM spectrum of a high-quality CuCl thin film with a thickness of 268 nm. The measurement temperature is 5.6 K. The spectrum of the incident laser is also shown by the dashed gray line. E_T and E_L indicated by vertical dotted lines at 3.2022 eV and 3.2079 eV show the transverse and longitudinal exciton energies of bulk crystal, respectively [9]. The DFWM spectrum exhibits two main structures. One lies below E_T and contains several peaks, and the other lies around E_L. This result is different from those in CuCl thin films grown by the ordinary MBE method without electron beam irradiation, where only two peaks are observed. Fig. 2(b) and (c) shows the complex radiative corrections as functions of the thickness in an exciton–radiation coupled system [16]. The real parts of radiative correction correspond to the eigenenergies including the radiative shift shown in Fig. 2(b), in which the energy at the intersection of the calculated curve and a horizontal solid line corresponds to the eigenenergy at the film thickness of 268 nm. The eigenenergies for $n=2$, 3, 5–7 precisely coincide with the energies of the peaks shown in the DFWM spectrum in Fig. 2(a). The structure at 3.2086 eV contains the mode for $n=1$ as well as for $n=2$ due to small differences between these energies, while no structure is observed at the energy for $n=4$. The imaginary parts of radiative corrections shown in Fig. 2(c) correspond to the radiative widths. The width for the excitonic state of $n=4$ is the largest at the thickness of 268 nm, and those for $n=3$, 5 are relatively large. The very large spectral width of the components at 3.1931 eV and 3.2101 eV in Fig. 2(a), which are assigned to the eigenenergies for $n=5$ and $n=3$, may reflect the large radiative width, while the component corresponding to $n=4$, for which much larger width is expected, is not observed due to too much broad spectral shape.

Since the peak energies of DFWM spectra reflect the real parts of calculated radiative corrections, the response times of DFWM should reflect the imaginary parts i.e. the radiative widths. Fig. 3 shows the result of delay time dependences of the TG measurement in the CuCl thin film [17]. It exhibits exceptionally short radiative decay time of as low as 100 fs, which is several orders of magnitude shorter than the typical excitonic radiative decay time, and a clear beating structure is shown in these decay curves. With regard to the first point, it is found that the fastest component in each observed curve is consistent with the calculated radiative decay time derived from the calculated radiative width of the corresponding state shown in Fig. 2(c). The calculated decay time τ_r is inversely proportional to radiative width γ and can be calculated from the relationship: $\tau_r=\hbar/2\gamma$ [18]. For example, the radiative decay times are 103 and 115 fs for the $n=5$ and $n=3$ states, respectively. Each decay profile agrees well with the result of the real-time calculation [17]. Regarding the second point, the clear beating structures in the decay curves reveal the high excitonic coherence extended to the entire volume of the sample up to higher-order states, despite a thickness over several hundred nanometers. For example, in the case of a thickness of 268 nm, the energy separation between the excitonic states of $n=1$