

# A study of novel nonthermal epitaxial technique of compound semiconductor using synchrotron radiation<sup>†</sup>

MITSUHIRO NISHIO,\* KAZUKI HAYASHIDA, TOORU TANAKA, QIXIN GUO AND HIROSHI OGAWA  
Department of Electrical and Electronic Engineering, Saga University, Saga 840-8502, Japan.  
email: nishiom@cc.saga-u.ac.jp; Phone: +81-952-28-8656; Fax: +81-952-28-8657.

## Abstract

ZnTe homoepitaxial growth has been investigated at room temperature using synchrotron radiation. Growth characteristics of the film such as thickness distribution and source transport rate dependence of the growth rate have been studied as also the effect of diethyltelluride/diethylzinc gas composition on the photoluminescence spectrum of the film. A sharply excitonic emission at 2.375 eV associated with shallow acceptors is observed and neither a donor–acceptor pair recombination nor a deep-level luminescence signal is detected in the spectrum of the film grown under nearly stoichiometric condition, which indicates that ZnTe films of good quality can be grown even at room temperature by this growth technique. We discuss the relationship between substrate temperature and photoluminescence spectrum of the film in relation to actual VI/II ratio near the growing surface.

**Keywords:** Synchrotron radiation-excited growth, low temperature growth, ZnTe, photoluminescence property.

## 1. Introduction

Lowering of temperature to grow thin film has become important for fabrication of future semiconductor devices such as quantum-effect devices. Photo-excited growth is one of the leading candidates for low-temperature growth which also results in low damage. Synchrotron radiation (SR) has a high photon flux density in the vacuum ultraviolet region, and hence it decomposes virtually all reactants efficiently. Furthermore, irradiation enhances the surface migration of adsorbed species. These features make the SR-excited growth a promising new nonthermal technique. Several attempts have been made in using SR light to perform photo-excited deposition of elemental semiconductors<sup>1–11</sup> or metals.<sup>12–19</sup> Interestingly, the epitaxial growth of elemental semiconductors such as Si<sup>1–10</sup> and Ge<sup>9</sup> has been achieved at low growth temperature using SR light. Some reports<sup>20–31</sup> on the synthesis of compound semiconductors using different gas sources exist as compound semiconductors are important materials for optoelectronic devices. This technique will be useful for use in the patterned deposition of compound semiconductors such as the preparation of photonic crystals and quantum-effect devices.

Thus the purpose of this study is to deal with SR-excited growth of ZnTe as an example for compound semiconductors. We describe herein the growth characteristics and photoluminescence (PL) properties of the deposited films.

## 2. Experimental

The growth experiment was carried out using the SR beam line, BL8A, constructed at the UVSOR Facility of the Institute for Molecular Science, Japan. The beam line supplies only white light.

\* Author for correspondence.

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**Table I**  
**Growth conditions**

Substrate	(100) ZnTe
Source materials	Diethylzinc (DEZn) Diethyltelluride (DETe)
Transport rate	0.05~1 $\mu\text{mol}/\text{min}$
Carrier gas flow rate	0.25 sccm for each source
Total pressure	$10^{-5}$ ~ $10^{-4}$ torr
Substrate temperature	mainly room temperature
Carrier gas	hydrogen
Incident SR beam	sample surface perpendicularly
Area exposed with SR	6 mm in diameter
Photon flux b integrated over the wavelength 5 to 1500Å	$6 \times 10^{15}$ photons/mA·min·cm <sup>2</sup> for the irradiated center area on the sample

Our growth apparatus<sup>25</sup> consists of a reaction chamber, load-lock chamber and differential pumping system. The differential vacuum pumping system prevents reaction gas from flowing in the storage ring. The incident SR beam is irradiated perpendicular to the sample surface without window. (100) ZnTe substrates were used. Diethylzinc (DEZn) and diethyltelluride (DETe) were used as source materials, and were fed independently into the chamber together with hydrogen carrier gas by means of mass flow controller and variable leak valve. Carrier gas flow rate was kept at 0.25 sccm for each source. The deposition was carried out at very low pressure between  $10^{-5}$  and  $10^{-4}$  torr. The substrate temperature was mainly the room temperature. The area exposed to SR, which is limited by the size of aperture in differential pumping system, was 6 mm in diameter. The photon flux integrated over the wavelength from 5 to 1500Å was calculated to be  $6 \times 10^{15}$  photons/mA·min·cm<sup>2</sup> for the irradiated center area on the sample. The growth conditions are summarized in Table I. The characteristics of the deposited film have been investigated by means of stylus step profiler, Auger electron spectroscopy, high-energy electron diffraction (RHEED) and PL. If the film is too thin, PL signal from substrate will dominate. PL measurements on ZnTe films of 2–2.5  $\mu\text{m}$  thickness were carried out at 4.2 K to avoid the effect of the substrate. The growth rate is defined as the maximum thickness of the film normalized by total irradiation dose which is represented by a product of electron current (mA) and exposure time (min).

### 3. Growth characteristics of ZnTe films

Figure 1, a typical SR deposited film, shows the deposition of the film clearly on the substrate. The deposition takes place at room temperature which is much lower than that required for thermal decomposition of source materials, namely, about 200°C for DEZn<sup>32</sup> and about 380°C for DETe<sup>33</sup> in the gas phase. The area of the deposition is almost equal to the size of the SR incident beam and no deposition takes place in the nonirradiated part. This suggests the possibility of adapting SR-excited growth of ZnTe for use in the patterned deposition, which is useful from the application point of view.

Figure 2 shows the thickness profile of ZnTe film grown with total irradiation dose of  $2.17 \times 10^5$  mA·min in the vertical direction. The deposition thickness depends strongly upon the distance. It is well known that there is a strong intensity distribution of SR beam in the vertical direction (i.e. in the direction perpendicular to the plane of the SR orbit). The intensity has a peak at the center

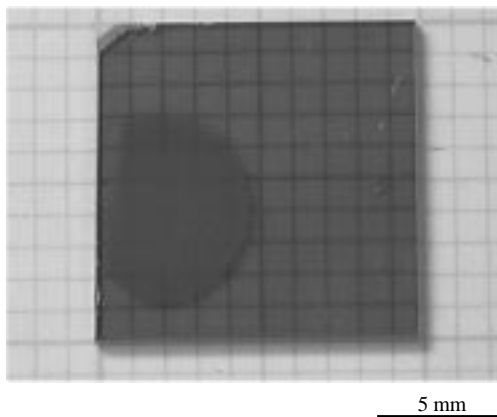


FIG. 1. ZnTe film on the substrate. The left side of the substrate is covered with tantalum holder to measure the thickness profile easily.

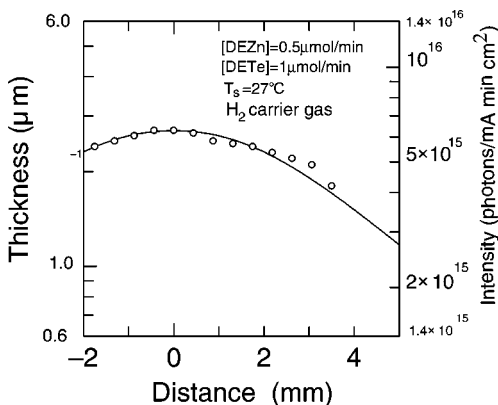


FIG. 2. A typical trace measured with a stylus step profiler. The solid line represents the light intensity calculated theoretically as described in the text.

of the SR beam and decreases away from the center along the vertical direction. The intensity distribution of SR beam, between 5 and 1500 Å, shown by solid line, is considered the wavelength region. The thickness is almost proportional to the intensity of the SR beam. Since the total power of the incident beam is less than 0.3W, the temperature rise of the substrate due to SR irradiation is negligible. Thus, the deposition due to thermal excitation may be excluded. Under SR irradiation, several phenomena such as photo-stimulated evaporation of the film, as shown in SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> films,<sup>34</sup> the formation of blocking layer<sup>12</sup> and also the deposition of the film due to decomposition of adsorbed molecules or gas molecules with the help of SR<sup>9</sup> have been observed so far. As regards photo-stimulated evaporation, ZnTe as well as ZnSe<sup>26</sup> are unaffected by SR irradiation. Also, since the carbon-free ZnTe films can be obtained as stated later, the deposition process of ZnTe should not be considered a growth suppression effect due to the formation of blocking layer as pointed out in the SR-excited deposition of Al, where Al deposition is suppressed by the formation of AlC layer.<sup>12</sup> The decomposition of gas molecules by SR (gas phase excitation) may also be negligible, since the area of the deposition is almost the same as that of SR incident beam. Thus, the process associated with the adsorption of DEZn and DETe molecules followed by decomposition due to SR irradiation (surface excitation process) will be essential for ZnTe growth, in view of very low pressure.

Figure 3 shows the relationship between growth rate and source transport rate. When DEZn transport rate is maintained at 0.1 μmol/min, an almost linear relationship is obtained, indicating that the rate-limiting step is due to the supply of DETe. When the transport rate of DETe is maintained at 1 μmol/min, the growth rate increases rapidly with increasing DEZn transport rate. As shown by open circles, growth rate is controlled by DMZn transport below 0.1 μM/min. On the other hand, growth rate is perfectly governed by DETe transport rate of 1.0 μM/min. The middle region (i.e. 0.5 μM/min) corresponds to stoichiometric conditions. It eventually gets saturated at around 0.5 μmol/min. These results indicate that the adsorption coefficient of DEZn is high compared to DETe at room temperature. Thus, at 1 μmol/min for DETe, the transport rates of DEZn of 0.1, 0.5 and 1 μmol/min correspond to a Te-rich condition, nearly stoichiometric and Zn-rich condition, respectively.

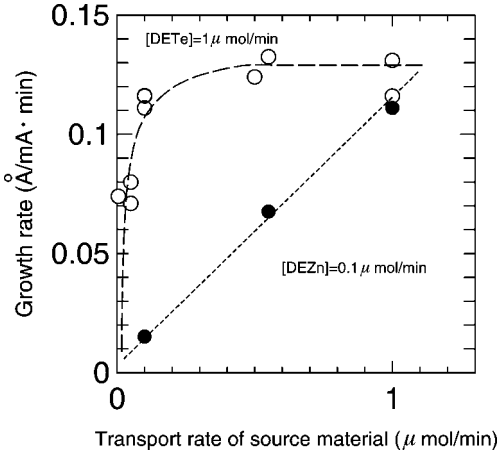


Fig. 3. Dependence of the growth rate on the source transport rate at 27°C substrate temperature.

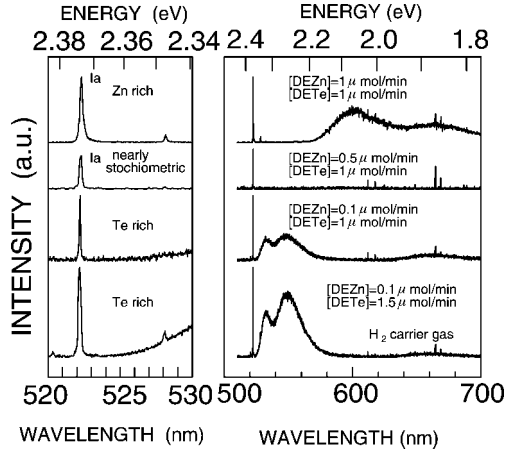


Fig. 4. PL spectra of ZnTe films for various source transport rates with the substrate temperature maintained at 27°C.

#### 4. Photoluminescence properties of ZnTe film

Auger electron spectroscopy of the deposited film exhibits only the signals relating to ZnTe. It is to be noted that no signal is detected with regard to carbon in the film. It is expected that both DEZn and DETe molecules decompose and hydrocarbons desorb effectively from the surface by the irradiation of SR. An analysis of RHEED patterns of deposited ZnTe films drew the following conclusions: At low growth rate, say  $\sim 0.7 \text{ \AA/mA}\cdot\text{min}$ , epitaxial film can be obtained independent of the transport rate ratio of DETe to DEZn. For high growth rate such as  $\sim 1.2 \text{ \AA/mA}\cdot\text{min}$ , it seems difficult to obtain the epitaxial film when growth is carried out under Zn-rich condition. When growth is carried out under Te-rich or nearly stoichiometric condition, on the other hand, ZnTe film grows epitaxially. Thus, the homoepitaxial ZnTe film is attainable even at room temperature for such a high growth rate.

It is interesting to investigate the PL spectrum of the film deposited by SR-excited growth because very little work with such luminescence has so far been reported. In order to investigate the influence of DETe/DEZn composition on PL spectrum of the film, we have selected the films with almost the same growth rate. As shown in Fig. 4, PL property of ZnTe film strongly depends upon the DETe/DEZn gas composition. The PL spectrum of the film grown under Zn-rich condition exhibits strong deep-level emissions with two broad bands together with  $I_a$  line.  $I_a$  line is attributed to shallow acceptors, namely, Li, Cu and Na.<sup>35</sup> The deep-level luminescence may be due to defects such as vacancy-chlorine complex and the one obtained here can be found in the experimental results of Tews *et al.*<sup>36</sup> who have attempted laser-induced diffusion in ZnTe with Cl. Thus, the quality of the film deteriorates under Zn-rich condition. Under nearly stoichiometric condition,  $I_a$  peak is observed and neither a donor-acceptor pair recombination nor a deep-level luminescence signal is detected even in the film grown at room temperature. Similar feature for PL spectrum has been reported on ZnTe homoepitaxial layers grown under optimum conditions by molecular beam epitaxy<sup>37</sup> and metal organic vapor phase epitaxy,<sup>38</sup> where the growth has been carried out at 330°C and 340°C, respectively. Hence, it can be said that ZnTe films of good

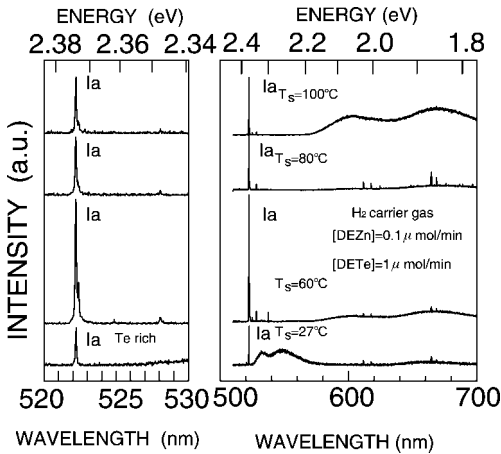


FIG. 5. PL spectra of ZnTe films deposited by varying substrate temperatures.

quality can be obtained at much lower substrate temperature than those of molecular beam epitaxy and metal organic vapor phase epitaxy. The PL spectrum of the film grown under a Te-rich condition shows donor–acceptor pair bands together with  $I_a$  line. A Te-rich condition may lead to the contamination of shallow acceptor and donor impurities related to these emission bands.

Figure 5 shows the PL spectra of ZnTe films deposited for different substrate temperatures. The films grown at 60°C and 80°C exhibit a strong  $I_a$  peak. Donor–acceptor pair bands are not detected in the spectrum, but are observed clearly in the spectrum of the film deposited at 27°C. PL spectra of these films resemble the one corresponding to nearly stoichiometric condition. However, a further increase in substrate temperature (100°C) induces enhancement of the deep-level luminescence, which resembles the one corresponding to the spectrum of the film obtained under Zn-rich condition. We have already reported that the growth rate decreases with increasing substrate temperature. This behavior will be closely related to decrease in the adsorbed molecules with respect to DETe rather than DEZn with increasing substrate temperature. Thus, the PL properties of the films as a function of substrate temperature may be closely related to the fact that the actual VI/II ratio near the growing surface becomes lower with increasing substrate temperature.

## 5. Conclusions

We have described the SR-excited growth of ZnTe as an example of compound semiconductors. The growth characteristics and PL properties of the deposited films have been established. A sharp  $I_a$  line associated with shallow acceptors is observed and neither a donor–acceptor pair recombination nor a deep-level luminescence signal is detected in the spectrum of the film grown under the nearly stoichiometric condition, indicating that ZnTe films of good quality can be obtained even at room temperature. Strong deep-level emission bands centered at 1.85 and 2.1 eV related to defects such as vacancy–impurity complex become prominent with increasing DEZn transport rate. These bands are also detected at high substrate temperature. This will be due to the fact that actual VI/II ratio near the growing surface becomes lower with increasing substrate temperature.

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