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Two-Beam Photoacoustic Analysis of ZnSe/GaAs Grown by MOCVD

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〈Abstract〉

A two-beam excitation photoacoustic spectroscopy (PAS) system with a piezoelectric transducer (PZT) as the detector has been utilized in the study of the optical properties of a wider-bandgap material ZnSe grown on a narrower-bandgap material GaAs substrate. Samples were grown by metal organic chemical vapor deposition (MOCVD) using dimethylzinc and diethylselenide as source materials of ZnSe crystal on *p*, *n*-, and semi-insulating GaAs(100).

The photoacoustic spectra have a sharp dip near the bandgap energy of ZnSe. The intensity of the PA signal is highly dependent on the conduction type of the substrate.

MOCVD 법으로 생장한 ZnSe/GaAs의 Two-Beam 광음향효과

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〈요 약〉

검출기로 압전소자(PZT)를 사용한 two-beam 이기 광음향 분광시스템을 써서 narrower-bandgap 물질 GaAs 기판위에 생장된 wider-bandgap 물질 ZnSe의 광학적 성질을 조사하였다. 시료는 ZnSe 실험의 원료물질로써 dimethylzinc 와 diethylselenide 를 써서 유기금속화물 기상반응법(MOCVD)으로 *p*-, *n*-, 및 반절연성 GaAs(100)기판위에 생장시킨 것이다.

광음향 스펙트럼은 ZnSe의 bandgap에너지 근처에서 sharp dip을 보였다. 광음향 신호의 세기는 기판의 전도형에 의존하였다.

I. Introduction

Photoacoustic spectroscopy (PAS) has contributed to the study of the optical properties of solids in recent years.[1-4] This technique is powerful not only in the measurement of the optical absorption spectra of powdered samples[5], but also in the study of the surface state and nonradiative relaxation processes of various kinds of materials. The photoacoustic spectrum, however, is an emission spectrum of total generated heat involving various phonon states. To study the nonradiative recombination process quantitatively, it is necessary to compare and analyze the photoacoustic spectrum together with the luminescence spectrum.

When an intensity-modulated light beam is

absorbed by a sample, the excitation energy is converted to thermal energy entirely or partially. In conventional photoacoustic spectroscopy, the generated heat which is periodically deposited in the sample is transferred to an optically nonabsorbing gas by thermal conduction, and this causes pressure oscillations in the gas at the modulated frequency. These pressure oscillations are detected by a microphone and constitute the photoacoustic signal. But this scheme is not applicable for thin larger-bandgap epitaxial layers grown on smaller-bandgap substrates because the thickness of the epitaxial layer is relatively thin and the band gap energy of the substrate is smaller than that of the epitaxial layer.

Recently, an altenative photoacoustic technique has been developed utilizing a piezoelectric transducer (PZT) attached directly to the sample with low-viscosity epoxy.[6] The absorption-induced periodic heating causes the samples to develop thermal stresses and strains to an electronic signal.

In this paper, we report on the photoacoustic spectra of 1.2μm-thick undoped ZnSe grown on p-, n-, and semi-insulating GaAs substrates by the metal organic chemical vapor deposition (MOCVD) method using a new two-beam photoacoustic spectroscope. These samples were grown simultaneously at a substrate temperature of 380°C under atmospheric pressure using dimethylzinc (DMZn) and diethyselenide (DESe) with a growth rate of about 0.24μm/h.[7]

Ⅱ. Experiment

The experimental arrangement of the two-beam PZT-PAS measurement system is shown is shown in Fig. 1. Light from the 100W tungsten lamp and the 100W high pressure Hg-lamp simultaneously irradiate the sample which is immersed in ethanol. The modulation frequency of the tungsten light is 8 Hz. In order to normalize the PA signal against the intensity of the excitation light, the chopped tungsten light is dispersed in a monochromator (f−25cm) and then divided into two parts by a quartz partial mirror selectively vacuum-coated with aluminum. The main beam transmitted through the quartz plate is incidented on the sample and reflected beam is detected with a Si-PIN diode. The signals from the sample (PA signal) and photodiode are amplified by two lock-in amplifiers, divided and recorded. Here, the PA signal intensity against excitation light intensity is assumed to be linear. The 440nm dc monochromatic light from the Hg-lamp, via the monochromator (f=25cm), is superimposed on the sample together with the chopped tungsten light. The structure of the PAS cell is shown

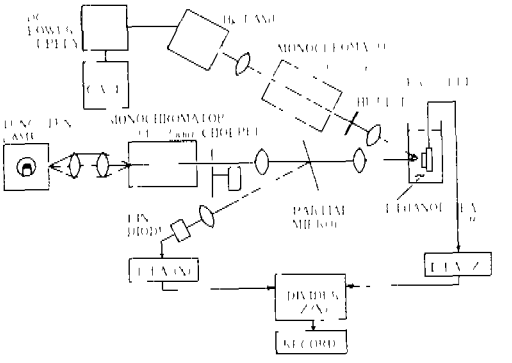

Fig. 1. Block diagram of the two-beam PZT-PAS system.

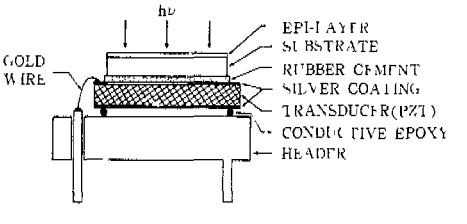

Fig. 2. Photoacoustic sample. Here, the epitaxial layer is ZnSe and the substrate is GaAs. The photoacoustic signal is detected from this sample which is immersed in ethanol.

in Fig. 2.[8] To allow for the bending mode oscillation, the four corners of the PZT are glued by conductive epoxy (EPOTEK H-20*E*, two-solution type). The wafer sample is mounted on the PZT by rubber cement. To pick up the PA signal from the epi-layer surface effectively, the PAS cell is immersed in ethanol which acts as a pressure oscillation transfer medium.

Ⅲ. Results and Discussion

When water or methanol is utilized instead of ethanol, the form of the PA spectrum is almost the same except for only a slight difference in signal intensity (Fig. 3). When a solution is not used (in this case, air plays the role of the pressure oscillation transfer medium), the PA signal intensity is only about one thousandth as great. The PA signal increases abruptly near 465nm (2.67eV) due to excitation across the intrinsic band gap. Periodic heat due to light absorption by the sample surface expands the ethanol explosively and makes a pressure pulse. This pressure pulse spreads out over the whole of the ethanol and is transferred via the rubber cement which presents a low acoustic impedance match (the acoustic impedance ρC = the density of material ρ × the velocity of sound in the material C, $N \cdot s \cdot cm^{-3}$) (Table 1). The rubber cement allows the transducer to perform bending mode oscillation following the transferred pressure pulse. Then, the PA signal arises between the two sides of the transducer. The rubber cement plays the role of a low pass filter and decreases the intensity of the direct acoustic wave transmitted through the sample wafer.

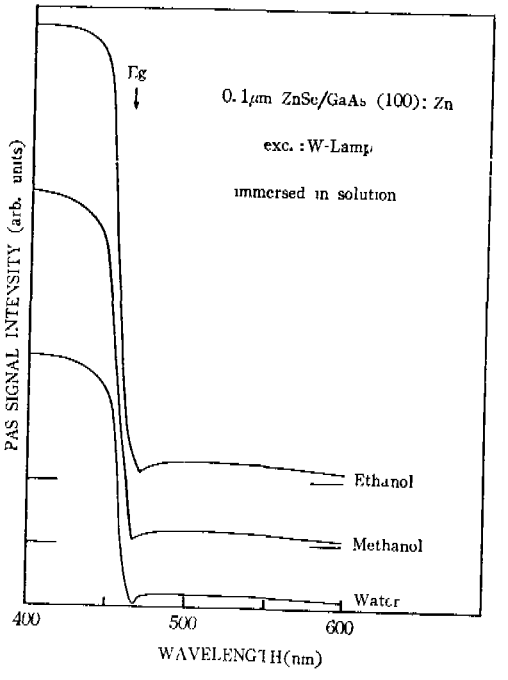

Fig. 3. Photoacoustic spectra of 0.1μm-thick ZnSe/GaAs using methanol, water, and ethanol as the pressure oscillation transfer medium. These spectra, obtained using only tungsten light as the excitation source, are not normalized.

Table 1. The acoustic impedances of the constituents of the PAS cell.

	density ρ (g/cm³)	velocity of sound, C (cm/sec)	acoustic impedance, ρC ($N \cdot$sec/cm³)
ZnSe	5.3	4.4×10^5	23.3
GaAs	5.3	5.0×10^5	26.5
rubber cement	1.1	1.3×10^5	1.43
PZT	7.5	5.0×10^5	37.5
ethanol	0.79	1.2×10^5	0.95

Photoacoustic spectra of 1.2μm-thick ZnSe grown on *p*-, *n*-, and semi-insulating GaAs (100) substrates are compared in Fig. 4. In all three cases, (a), (b), and (c), the PA spectrum excited by tungsten light only (dotted curve) has a relatively high intensity in the region of wavelength shorter than 465nm, but is hardly detected for regions of longer wavelength excitation. When light of 440nm from the Hg-lamp dispersed through a monochromator irradiates the PAS sample, the PA signal (solid curve) is reduced to about one tenth for shorter wav-

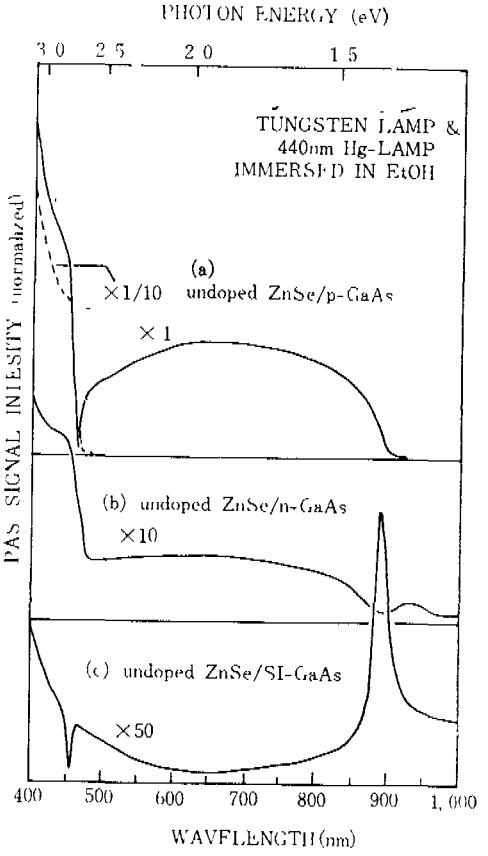

Fig. 4. Photoacoustic spectra of 1.2μm-thick ZnSe grown on different conduction types of GaAs. The solid curves are the two-beam photoacoustic spectra, while the dotted curve is the photoacoustic spectrum with tungsten light only.

elength excitation, while on the other hand it appears for longer wavelength excitation. When the 440nm light is turned off, the PA signal for longer wavelength excitation decreases rapidly and disappears. And it appears at the original level when the light is again turned on. A sharp dip appears near 465nm. The PA spectra are different for different conduction type substrates. Especially apparent is the relatively large peak near 885nm in the case of the semi-insulating GaAs substrate.

When the 440nm dc Hg-light is irradiated, the characteristics of the PA spectra (Fig. 4) are as follows.

(1) *Reduction of the signal intensity for λ_{ex} (excitation wavelength of the tungsten light) <465nm.* Because of the steady state excitation by dc light, the electrons in the ZnSe epi-layer are excited at a constant rate. Therefore, a small percentage change in the excited electron concentration takes place due to irradiation by the pulsed tungsten light. This induces a small PA signal intensity.

(2) *Appearence of the PA signal for λ_{ex}> 465nm.* The dc light transmitted through the ZnSe epi-layer supplies energy continuously to excited electrons in the GaAs substrate. For decay to ground state, the excited electrons cannot but give up energy through thermal collisions, and this constitutes the PA signal which may originate from impurities and other defects in the ZnSe and GaAs.

(3) *Functions of the rubber cement and ethanol.* The photoacoustic signal transmitted to the GaAs substrate is about 95% reflected and about 5% transmitted at the interface between GaAs and rubber cement which has an acoustic impedance of about 1/20 that of GaAs. In the GaAs substrate, there is a resonance between the superimposed pulsed PA signal and the reflected signal. This resonant signal is transferred to the transducer through the ethanol which is much less compressible than air. The rubber cement acts as a low pass filter and the ethanol as a pressure oscillation transfer medium.

(4) *Apprearence of a dip.* The dip represents the room-temperature blue emission attributed to the recombination of free holes with donor electrons[9] in the ZnSe epi-layer, since any absorbed energy which is re-radiated as luminescence does not contributed to the photoacoustic signal.[10]

(5) *Difference in intensity with different conduction type substrates.* Diffused Ga conc-

centration in the ZnSe from the GaAs substrate has been reported, by vapor phase epitaxy, to be higher than the diffused As concentration.[11] Therefore, the undoped ZnSe grown on GaAs appears to be *n*-type due to the excess Ga atoms which will act as donors in the ZnSe[12] (1×10^{16} cm^{-3} by MBE,[13] MOCVD[14]). So, the samples (a), (b), and (c) in Fig. 4 will be *n*-ZnSe/*p*-GaAs, *n*-ZnSe/*n*-GaAs, and *n*-ZnSe/SI-GaAs, respectively. Utilizing the energy-band model for an ideal abrupt heterojunction proposed by Anderson[15], a step in the conduction and valence bands exists at the heterojunction due to the difference in electron affinity and band gap energy between the ZnSe and the GaAs. But there is no spike or notch at the interface of the conduction bands because the electron affinity of the smaller-bandgap material GaAs substrate is smaller than that of the larger-bandgap material ZnSe epi-layer(Fig. 5) (Tab. 2). The intensity of the PA signal with or without the dc light is in the order of (a), (b), and (c). This means that the dc light induces a constant rate diffusion of the minority carriers and there is no change in the PA spectra. On the other hand, the pulsed light induces a large percentage change in the minority carrier concentration, in other words, the current density at the interface is largest in the case of (a) and smallest in the case of (c). Therefore, a difference in signal intensities can be expected in accord with the discussion of (2). There is a considerable effect due to the GaAs substrate only in the case of (c), which is caused by the thermal energy generated from the Cr doped semi-insulating GaAs substrate.

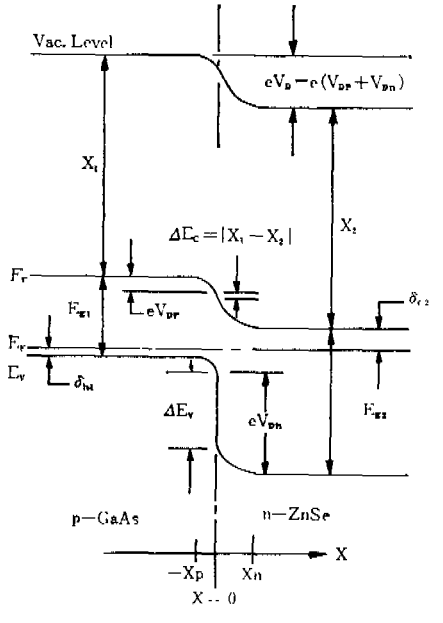

Fig. 5. Energy band diagram for the *p*-GaAs/*n*-ZnSe heterostructure.

Table 2. Properties of *p*-GaAs and *n*-ZnSe heterostructure.

	GaAs	ZnSe
E_g(eV, 300K)	1.43	2.67
χ(eV)	4.07	4.09
ε_r	13.18	9.14
m_{de}^*/m_o[16]	0.067	0.16
m_{dh}^*/m_o[16]	0.473	1.472
$p, n(cm^{-3})$	2×10^{18}	1×10^{16}
δh_1, δe_2(eV)	0.04	0.13
eV_{Dp}, eV_{Dn}(eV)	4.29×10^{-3}	1.236
x_p, x_n(cm)	1.77×10^{-7}	3.54×10^{-7}

Definitions of symbols: χ is the electron affinity; ε_r is the relative permitivity; $m_{de}^*(m_{dh}^*)$ is the density-of-state effective mass for electrons (holes); V_D is the diffusion potential: x is the transition region width.

In summary, we have found that the two-beam excitation photoacoustic spectroscopy system with a piezoelectric transducer as detector is useful for study of the optical properties of larger-bandgap and thin epi-layer grown on smaller-bandgap materials.

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