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Citation	Japanese Journal of Applied Physics. Part 1, 39(2A), 501-504 https://doi.org/10.1143/JJAP.39.501
Issue Date	2000-02
Doc URL	http://hdl.handle.net/2115/59642
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Type	article (author version)
Note(URL)	http://iopscience.iop.org/1347-4065
File Information	JJAP2000.pdf



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Intrinsic and Extrinsic Excitonic Features in MgS/ZnSe Superlattices Revealed by Microspectroscopy

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Microspectroscopy of luminescence and optical reflection properties was performed on MgS/ZnSe superlattices with the spatial resolutions of $\sim\mu\text{m}$ and $\sim 10\ \mu\text{m}$, respectively, to examine the origin of excitonic transitions. C1-HH1 well-defined excitonic peaks which originate from multi-monolayer (ML) variation of 4~5 ML height, formed predominantly at the ZnSe surfaces of MgS/ZnSe heterointerfaces, were found to make a significant contribution to the optical spectra. The detailed identification of these inhomogeneous C1-HH1 excitonic peaks and intrinsic C1-LH1 excitonic peaks, which are close in energy levels, is discussed on the basis of results of the present microspectroscopy studies and with respect to the temperature dependence of the luminescence spectra.

KEYWORDS: metalorganic vapor phase epitaxy (MOVPE), MgS, ZnSe, superlattice, excitonic property, microspectroscopy, localize, interface homogeneity, exciton transfer

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1. Introduction

Excitonic properties in wide band gap II-VI semiconductors remain very attractive targets for exploration from the viewpoint of both basic physics and their application. The binding energies of excitons in II-VI semiconductors tend to be larger than those in III-V semiconductors. The binding energy of ZnSe, for example, is 17.4 meV,¹⁾ and this value is almost four times as large as that of GaAs, 4.2 meV.²⁾ Introducing the quantum confinement effect, further enhancement of the exciton binding energy³⁾ and the oscillator strength⁴⁾ is expected. MgS and ZnSe have the largest energy gap difference among II-VI semiconductors which are closely lattice matched to GaAs substrates. Therefore, strong carrier confinement to the well layer is expected. We have reported the excitonic luminescence from MgS/ZnSe superlattices structures (SLs) up to room temperature.⁵⁾

In comparison with III-V semiconductors, however, smaller exciton Bohr diameters in II-VI semiconductors (~ 70 Å in bulk ZnSe) accompanied by stronger excitonic effects give rise to difficulties in discriminating intrinsic excitonic transitions and extrinsic features that arise from inhomogeneity in SLs. In this study, optical investigations of excitonic properties in MgS/ZnSe SLs were carried out using microreflection and micro-photoluminescence (μ -PL) spectroscopy. It is shown that the observations of energy separations of the exciton peaks close to C1-HH1 and C1-LH1 splitting, and well-defined absorption lineshapes, do not necessarily guarantee the identification of the origin of excitonic transitions. A similar splitting of exciton features originating from multi-monolayer (ML) variation of heterointerfaces is shown to be possible, which requires more comprehensive examination to determine the origin of excitonic transitions. Spatially resolved examination with microspectroscopy enables us to obtain highly suggestive information about the origin of excitonic transitions, and cross-sectional observation using a transmission electron microscope (TEM) and surface observation using an atomic force microscope (AFM) are performed in

order to provide information on the formation of multi-ML variations and their distributions. The temperature dependent shift of the excitonic origin is also discussed.

2. Experimental

MgS/ZnSe SLs were grown by horizontal atmospheric-pressure metalorganic vapor phase epitaxy (MOVPE) on semi-insulating GaAs (001) substrates at a substrate temperature of 450°C. More detailed growth conditions including interface purging effects on the quality of heterointerfaces are given elsewhere.^{5,6)} For μ -reflection spectroscopy, a halogen lamp was used as an incident light source, of which the scope area was approximately 30 μm x 30 μm . The 325 nm line of a He-Cd laser was used as an excitation source for μ -PL spectroscopy. The spatial resolution was ~ 3 μm in full width at half-maximum luminescence spot intensity distribution, which may be limited by carrier diffusion. The sample temperature was controlled between 10 K and room temperature.

3. Results and Discussion

Figure 1(a) shows the reflectance spectra of MgS(25 Å)/ZnSe(57 Å) SLs with 18 periods at 10 K. The solid line denotes the measured reflectance spectrum and the dotted lines the Gaussian exciton absorption lineshapes determined in order to give the best fit to the experimental reflectance spectrum which exhibits considerably sharp structures at around 430 nm. The details of the fitting method are given in ref. 7; and three excitonic absorptions were taken into account in the fitting procedure. The two downward arrows labeled C1-HH1 and C1-LH1 indicate the calculated excitonic transition energies related to heavy holes and light holes, respectively. Calculation of the excitonic transition energies in MgS/ZnSe SLs was performed with the following parameters: a ZnSe energy gap of 2.82 eV, and effective masses of $m_c^*/m_0 = 0.147$, $m_{\text{HH}}^*/m_0 = 0.6$, and $m_{\text{LH}}^*/m_0 = 0.31$ for ZnSe. The conduction band

offset of 0.67 eV and the valence band offset of 1.85 eV,⁸⁾ which were evaluated from X-ray photoelectron spectroscopy (XPS) measurements, were used. In the theoretical calculations, strain effects and excitonic binding energies calculated using the variational method were also considered.⁷⁾ Another excitonic absorption peak in the shorter wavelength region, tentatively attributed to the higher subband excitonic transitions, is broader and hardly observed at room temperature. Therefore, hereafter we will focus on the two peaks in the longer wavelength region.

The energy separation of the two peaks in the longer wavelength region in Fig. 1(a) is 37 meV, which is slightly larger than that of C1-HH1 and C1-LH1 transitions, ~28 meV. To examine the origin of these excitonic peaks, spatially resolved μ -reflection measurements were performed. The reflectance spectra showed spatial variation and the relative intensity ratio of the two absorption peaks showed dependence on the measuring positions. In the extreme case, the absorption was noticeably stronger in the higher energy peak; an example is shown in Fig. 1(b). If structural fluctuation is assumed to be the origin of this energy separation, the formation of multi-ML variations of ~4 ML would be required.

Spatially-resolved reflection measurements were performed at room temperature at 30 μ m intervals to examine the spatial variation of the energy separation, and the results are shown in Fig. 2. The overall absorption peak shift originates from the total layer thickness variation caused by the gas flow in the horizontal MOVPE system. The two dominant excitonic peaks in the lower energy region shown in Fig. 1 are plotted at each measuring point. The horizontal solid lines indicate the C1-HH1 exciton transition energies calculated for the discrete 10~23 ML thicknesses of the ZnSe well layers. This figure reveals that the energy separation of the two excitonic peaks corresponds to a 4~5 ML difference in the well layer thickness and is kept constant in the relatively wide area of the sample. We confirmed that the average thickness of one period of SLs is reasonably constant by observing the clear SL

satellite peaks in X-ray diffraction measurements⁹⁾; therefore, the layer-by-layer thickness fluctuations among the well layers is sufficiently small.

On the basis of the above observations, the origin of excitonic transitions shown in Fig. 1 is primarily attributed to the extrinsic transitions caused by the 4~5 ML multi-ML variation formed at the heterointerfaces, and partially attributed to the C1-LH1 excitonic transition. A cross-sectional image was obtained by TEM and is shown in Fig. 3. MgS surfaces of ZnSe/MgS heterointerfaces are observed to be rather flat, whereas ZnSe surfaces of MgS/ZnSe heterointerfaces are likely to show a fluctuation of ~3 ML. Therefore, we attribute the optical properties caused by the interface fluctuations to the surface properties of ZnSe grown on MgS. AFM measurements of the ZnSe surface of SLs (2 μm x 2 μm) were performed to confirm the presence of the 4~5 ML multi-ML variation that is expected based on the optical characterizations by examining in more detail the surface morphology of ZnSe grown on the MgS layers. Figure 4 shows the AFM image of the topmost ZnSe layer of the MgS/ZnSe SLs and its cross-sectional profile. Surface structures of which the variation amplitude is about 4 ML, are unambiguously formed, as are structures with a lower variation amplitude. In contrast with the above TEM observation, the AFM lateral spatial resolution is low and terrace structures are not identified in this image, but the terrace area is sufficiently large compared with the spreading of the exciton wavefunction and the observation of the discrete excitonic peaks due to the difference of ~4 ML well thickness is possible. It is worth noting that the usual ML fluctuations are also present. Due to the limitation of the spatial resolution of the AFM system, it is difficult to make a detailed quantitative estimation of how these usual ML fluctuations influence the optical properties. It is likely that these structures contribute to the linewidth broadening of each discrete excitonic peak because the ML fluctuations are distributed within the spread of the exciton wavefunction.

As previously reported, Zn purging at the heterointerfaces is effective in reducing the

interface fluctuation.⁶⁾ Further optimization of the Zn purging conditions is under way, but some samples exhibited a flatter surface morphology with only a 1~2 ML fluctuation under AFM observation. In the MgS(17 Å)/ZnSe(43 Å) SL sample with 20 periods, the energy separation of the two absorption peaks was close to the energy difference between the C1-HH1 and C1-LH1 excitonic transitions and also to that corresponding to a ~3.5 ML well thickness variation. There is a striking difference between this sample and that discussed above, which is shown in Fig. 1. The ratio of the absorption coefficient of the higher energy peak to that of the lower energy peak is ~0.23, close to 1/3 of the ratio that is expected for the intrinsic transition in the transverse-electronic (TE) polarization. Moreover, the absorption coefficient ratio of the two peaks in the longer wavelength region exhibits a minimal measuring point dependence. These results show that in this sample, the excitonic properties are considerably more homogeneous from the viewpoint of excitonic absorption, and that the intrinsic features seem to be more significant.

We have examined the temperature dependence of PL spectra and one spectrum measured at 11 K is shown in the inset of Fig. 5. The dominant PL peak energy was about 6 meV less than the corresponding absorption peak. The integrated PL intensity ratio of the two peaks denoted by the arrows in the inset is shown in Fig. 5. From the higher temperature regime of >100 K, an activation energy of 29 meV was observed. This value is very close to the calculated energy separation of 34 meV between the C1-HH1 and C1-LH1 in this SL; therefore, the exciton accumulation process from the heavy-hole exciton state to the light-hole exciton state is assigned to be the origin of this activation energy. Below 100 K, however, experimental results begin to deviate from Boltzmann statistics (solid line in the figure), and have an almost constant ratio of ~0.1. This result is interpreted as follows. Luminescence is a consequence of relaxation processes; thus, it is sensitive to the potential fluctuations, particularly in systems with a small exciton Bohr radius. Despite the highly homogeneous

properties observed in the μ -reflection measurements, residual multi-ML variation is not completely suppressed and two energy regions with a different average well width are still formed. The almost constant PL intensity ratio measured independently of the temperature shows that these regions are sufficiently spatially separated to prevent the mutual transfer of excitons below 100 K. This shows that the regions of higher energy states formed by the monolayer fluctuations are estimated to cover $\sim 10\%$ of the entire area when the same optical transition rate is assumed for the C1-HH1 excitonic transitions in the two regions with different energy levels. At higher temperatures, the entire system reaches to thermal equilibrium, and luminescence via C1-LH1 transition in the dominant wider well region begins to contribute predominantly in the higher-energy spectra.

4. Conclusion

In conclusion, the excitonic features of MgS/ZnSe SLs were investigated in detail with microspectroscopy. Sharp excitonic peaks originating from the multi-ML variation of 4~5 ML height formed at the heterointerfaces, were clearly observed by spatially resolved spectroscopy. This observation showed that the multi-ML variation of heterointerfaces could appear as clear excitonic peaks of which the energy separation is very close to that of C1-HH1 and C1-LH1, and mask the intrinsic C1-LH1 excitonic transition that has a lower oscillator strength. In samples with better homogeneity, intrinsic excitonic absorptions dominated the spectra and intrinsic luminescence played the dominant role above 100 K. At temperatures below 100 K, however, extrinsic features remained dominant in the higher energy spectra, from which the monolayer flatness of the heterointerfaces was estimated to be $\sim 90\%$ of the entire area.

Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Nos. 10875064 and 09450119.

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Figure captions

Fig. 1 (a)(b). Microreflection spectra measured at 10 K. Two figures are obtained completely under the same condition except for the measuring point. Solid line denotes the experimental data, dotted lines denote the gaussian exciton absorptions assumed for the theoretical fit.

Fig. 2. Spatial distribution of absorption peak energies measured at room temperature. Spatial resolution is $\sim 30 \mu\text{m}$. C1-HH1 exciton transition energies for each well layer thickness are also shown. (horizontal lines)

Fig. 3. Cross-sectional TEM image of MgS/ZnSe SLs. Bright layers are MgS layers, and dark ones are ZnSe layers. It is shown that the multi-ML variations are predominantly formed on the ZnSe surfaces of MgS/ZnSe interfaces.

Fig. 4. AFM image of the topmost ZnSe layer. Surface fluctuations with the amplitude of ~ 4 ML are unambiguously observed. These structural features are possibly the origin of the discrete excitonic peaks observed in Fig. 1 and Fig. 2.

Fig. 5. Temperature dependence of integrated PL intensity ratio of two dominant PL peaks (see arrows in the inset). Above ~ 100 K, activation energy of 29 meV was obtained and was very close to the calculated energy separation between C1-HH1 and C1-LH1 excitonic transitions. Below ~ 100 K, however, almost constant ratio of ~ 0.1 was obtained, which was resulted from residual interface inhomogeneities. Temperature-driven transition of the origin of photoluminescence is clearly observed.

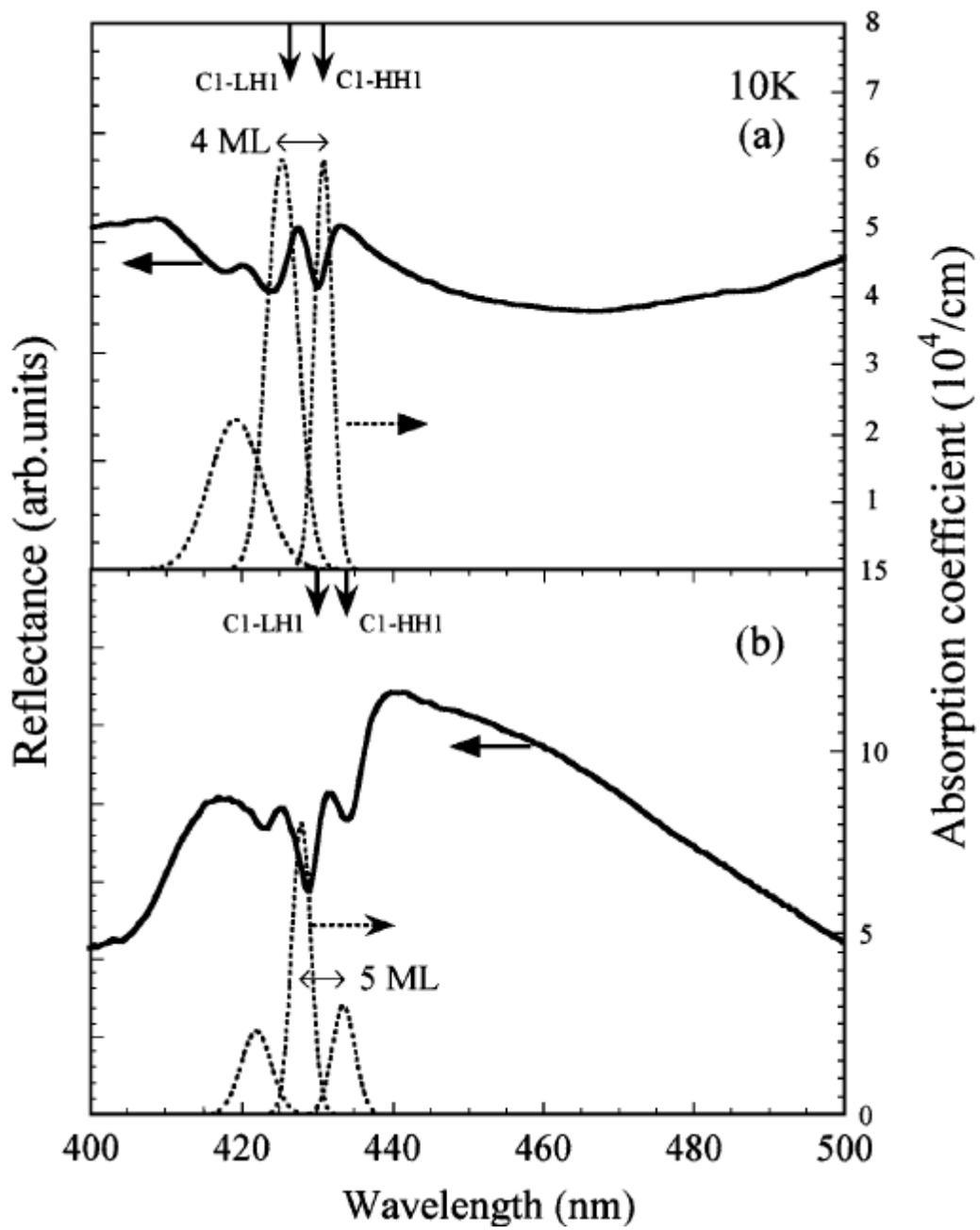


Fig. 1 H. Kumano *et al.*

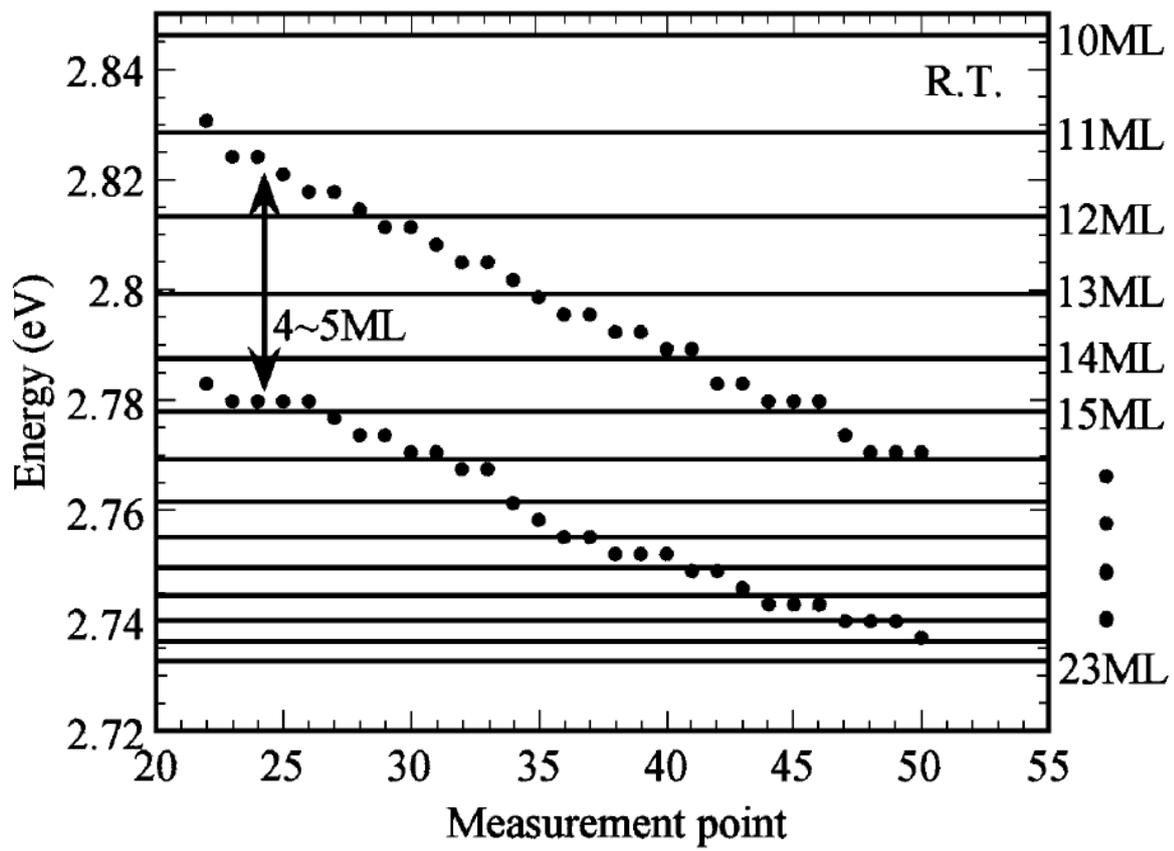


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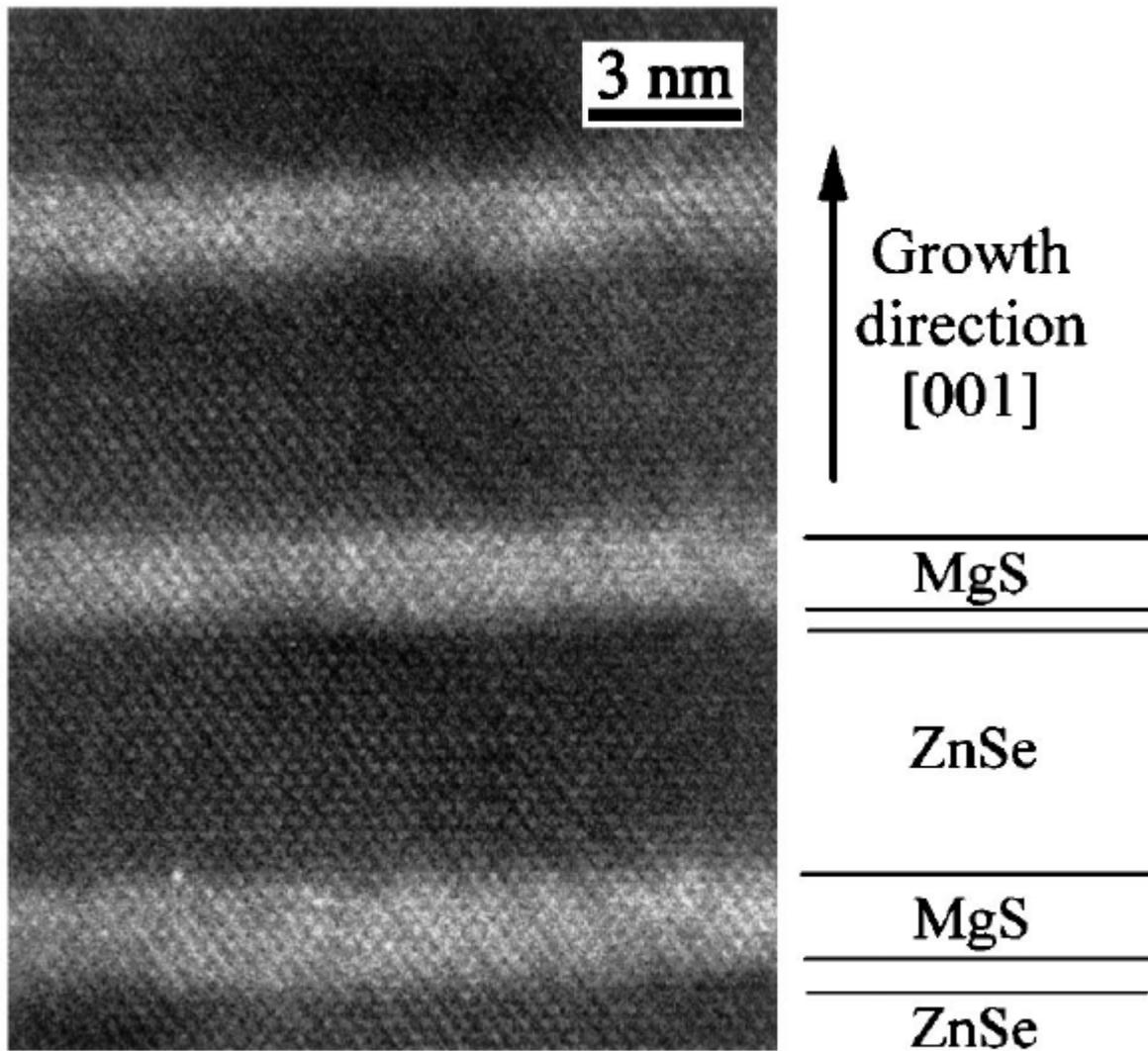


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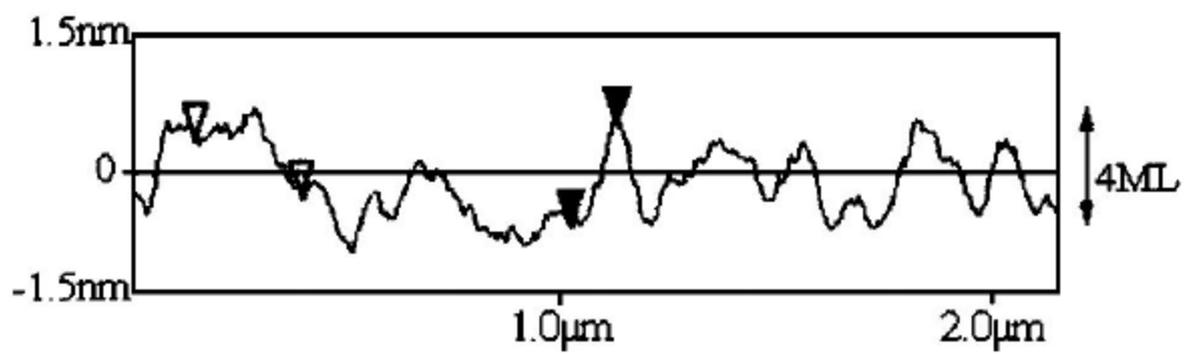
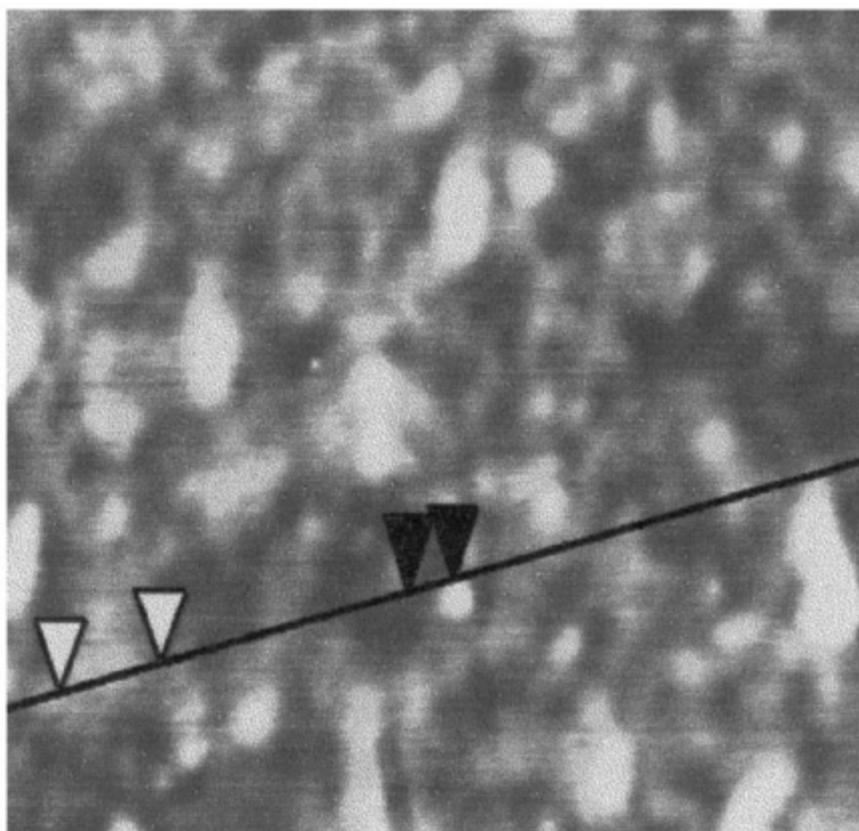


Fig. 4 H. Kumano *et al.*

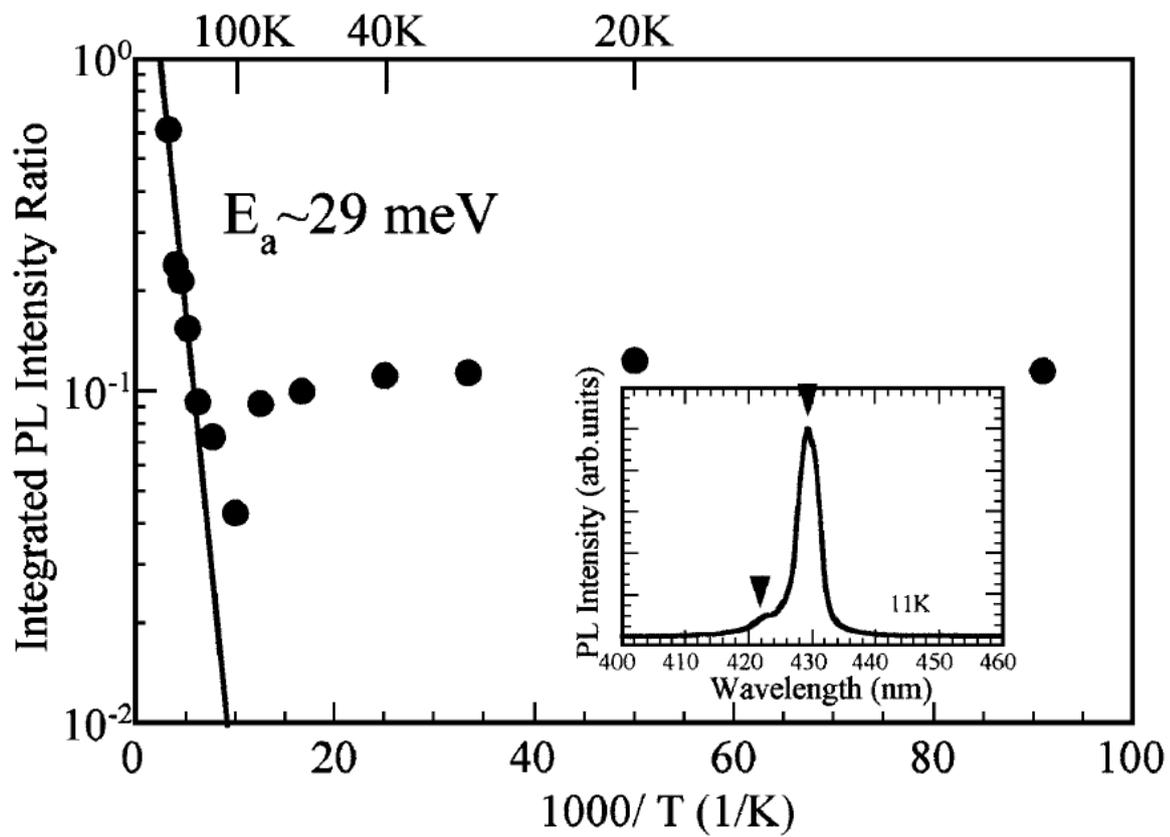


Fig. 5 H. Kumano *et al.*