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PHOTOLUMINESCENCE OF $ZnGe_{0.68}Si_{0.32}As_2$*

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ABSTRACT

A $ZnGe_{0.68}Si_{0.32}As_2$ layer epitaxially grown on GaAs was investigated for polarized photoluminescence. The luminescence peaks found around 1.5 eV were attributed to the GaAs substrate. Within our detection limits and with 2.4 eV excitation we could not detect photoluminescence in the energy range between 1.4 and 2.3 eV from the layer. The luminescence characteristics of the layer sample were the same as for the GaAs reference sample except for a small shift of the low energy peak towards higher energies at temperatures below 30 K. The luminescence polarization as a function of the excitation energy agrees with the curve found for the reference GaAs samples. The maximum luminescence polarization of 25% is not exceeded. The absorption behavior of the layer indicated an indirect bandgap at approximately 1.55 eV at 10 K. An indirect bandgap can account for the absence of luminescence, however such material is not suitable for an efficient spin polarized electron cathode.

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I. INTRODUCTION

The purpose of our investigation was to measure the luminescence polarization of the semiconductor material $ZnGe_{0.68}Si_{0.32}As_2$ (ZGSA). X-ray investigation confirmed the tetragonal chalcopyrite structure of ZGSA. Given the built-in lattice compression along the c-axis, the degeneracy of the valence bands at the Γ point is lifted. Due to selection rules and transition probabilities for the spin-polarized electrons, high polarization is expected for one of the valence-conduction band transitions. Table 1 gives a summary of the bandgap data for $ZnSiAs_2$ and $ZnGeAs_2$ at room temperature. The bandgap and the crystal field splitting of the mixed compound ZGSA have been calculated by linear interpolation from the data for the single compounds. Semiconductor bandgaps widen with decreased temperature. For example the bandgap of $CdSiAs_2$ widens by 90 MeV from 1.55 eV at room temperature to 1.64 eV at 10 K. Assuming a similar behavior for ZGSA we expect a bandgap at approximately 1.55 eV at 10 K.

II. SAMPLES

Sample 5 was a 10^{19} cm^{-3} Zn-doped GaAs wafer. ZGSA sample 9 was produced by the Research Triangle Institute (RTI). A 1 μm thick epitaxial ZGSA layer was grown by MOCVD (metal-organic chemical vapor deposition) on a 12.7 mm-diameter GaAs substrate (RTI 3–252). The information about the chemical composition was provided by RTI. We performed a standardless energy dispersive spectroscopy (EDS) analysis to probe the presence of the manufacturer-quoted constituents of the ZGSA sample. The stoichiometry was found to be Zn : Ge : Si : As = 31% : 18% : 4.6% : 46%($\pm$1%). The sample was etched for 4 minutes in 1 : 1 : 200 = 30%H_2O_2 : NH_4OH : H_2O at 22°C. However, only 2/3 of the sample was immersed into the

etchant to allow us to compare the etched and unetched surfaces. Sample 13 was originally a GaAs substrate exposed to the epitaxial MOCVD growth process (RTI 3–269). Subsequently the epitaxial layer was removed, and the wafer was anodized and stripped. This process removes approximately 50 nm from the GaAs surface. Sample 13 represents the same GaAs material used for the production of sample 9. The samples were mounted into a coldfinger dewar.

III. EXPERIMENT

Polarized photoluminescence spectra were acquired with a computer controlled standard setup. The sample excitation was performed in a near normal (<20°) incidence geometry. The laser polarization and luminescence analysis were achieved with linear polarizer/quarterwaveplate combinations. Three CW lasers: HeNe (1.96 eV, 0.5 mW), krypton (1.83 eV, 6 mW), semiconductor (1.66 eV, 1 mWcw) and a pulsed nitrogen pumped dye laser (2.4 eV, ~0.02 mW average power, $20H_z$) were employed for sample excitation. The laser foci were smaller than 0.4 mm. We adjusted the spectrometer slit widths to between 0.2 and 0.5 mm and used a holographic 1200 grooves/mm grating with a 2.5 nm/mm dispersion. The apparatus had a resulting slit resolution better than 3 MeV down to 1.7 eV. The spectrometer was calibrated with the 794.32 nm neon line. A −40°C cooled photomultiplier tube or cooled 1024 element diode array luminescence detection.

IV. RESULTS AND DISCUSSION

A. Spectra

We started by checking for the effect of the etching procedure on the emission spectra of the ZGSA sample. No difference was found between the luminescence data

of the etched and unetched parts. Both spectra showed a broad emission band E_1 at 1.47 eV. We conclude that the etching procedure did not affect the photoluminescence characteristics.

In Table 2 a comparison of the spectral features for GaAs reference sample 5 and the ZGSA sample 9 is given. The emission spectra at 100 K with HeNe excitation yielded E_1 at 1.47 eV for both samples. The intensity of sample 9 was a factor of 150 lower than that of sample 5. It appeared strange to find the same peak for these different samples. We expected luminescence at approximately 1.55 eV.

We proceeded to investigate the luminescence at 10 K. Table 2 summarizes all peak parameters. The HeNe excited spectra of samples 5 and 9 acquired at 10 K are dominated by a low energy transition E_1 at 1.47 eV. However, the ZGSA peak appears at 4 to 5 MeV higher energy. To the high energy side, the spectra show transition E_2 at 1.50 eV for both samples. The slightly different position of the ZGSA peak seemed to prove the origin of the emission from the layer. However, doubts arose due to the strong similarity between ZGSA and the GaAs luminescences with respect to position and line width. Also luminescence was expected at approximately 1.55 eV, rather than 1.47 eV at 10 K.

To verify that the observed luminescence was from the ZGSA layer, an additional investigation of the exact GaAs substrate material used for the production of the ZGSA layer was performed (our GaAs reference sample 5 could have had different doping thus leading to a slightly decreased peak position).

In Fig. 1 emission spectra for samples 9 and 13 are represented. Due to the shift of the ZGSA E_1 peak towards higher energies, E_2 nearly disappears in the high energy tail of E_1. Also, it is obvious from Fig. 1 that due to low emission intensities, the signal-to-noise ratio is poor for the ZGSA spectra. The emission spectra of the

substrate material sample 13 showed transitions E_1 and E_2 at 1.470 and 1.50 eV respectively. Again, as for the 100 K measurements, the luminescence intensities for the GaAs sample were high compared to those for the ZGSA sample, by a factor of approximately 600.

With 1.66 eV sample excitation of sample 13, both E_1 and E_2 appeared again at 1.470 and 1.50 eV, respectively. The twofold increase in luminescence intensity reflects the change in laser power. However, with 1.66 eV sample excitation, sample 9 behaved differently. Although E_1 and E_2 appeared unchanged at 1.475 and 1.50 eV, the intensity of the luminescence observed for sample 9 increased dramatically, by more than a factor of 80, compared to the HeNe excitation. Apparently the observed luminescence came not from the layer but from the underlying substrate. This was borne out by:

(1) Except for the small difference in the E_1 position, all emission spectra of samples 5, 9 and 13 are the same at all temperatures and excitation energies.

(2) Independent of the excitation energy, the peak intensity ratio I_1/I_2 is roughly 3 for all samples (a constant peak intensity ratio is typical for the luminescence spectrum of a particular material with given conditions). Therefore seeing the same ratio for the GaAs and the putative ZGSA spectra indicates that we actually see a GaAs spectrum in both cases.

(3) The emission intensity of the ZGSA sample is increased by a factor of 80 in changing from 1.96 to 1.66 eV excitation, even though the intensity from the bare GaAs substrate increased only by a factor of 2, reflecting the increased excitation power.

If we assume that the ZGSA layer only absorbs the exciting light and does not contribute any photoluminescence, then we understand the intensity increase with

reduced laser energy. The absorption of photons by a semiconductor depends on the photon energy. Lower energy photons have higher penetration depth due to a lower absorption coefficient near the bandgap region. Therefore we conclude that the increased emission intensity for 1.66 eV is due to reduced absorption of the exciting laser light by the ZGSA laser.

Another experiment helped clarify the situation. The photoluminescence intensity of the peak observed at 1.474 eV was recorded as a function of the excitation energy as shown in Fig. 2. Between 1.5 and 1.9 eV we see that normalized (to GaAs) reciprocal luminescence intensity, as a measure of the absorption coefficient displays a shallow slope which is indicative of an indirect transition in the region 1.5 to 1.6 eV. This value matches the predicted bandgap of 1.55 eV at 10 K quite well. The corresponding direct transition could not be detected between 1.4 and 2.3 eV. The important result here is the obvious presence of an indirect transition in ZGSA. It is highly unlikely to observe photoluminescence from an indirect bandgap semiconductor, and such material is not suited for photocathode application due to the phonon-assisted process involved.

A last experiment clarified the E_1 shift observed for the ZGSA sample. We investigated the peak positions of samples 9 and 13 excited with 1.83 eV as a function of the sample temperature. Below 30 K we can see in Fig. 3 the offset between the GaAs and the ZGSA E_1 peak. At higher temperatures, that splitting disappears, and we find no difference in peak position for the two samples up to 70 K. We conclude that the E_1 offset is a low temperature effect confined to temperatures below 30 K.

B. Polarization

The photoluminescence polarization data points are presented in Fig. 4. For all samples, the data points are lower than the theoretical limit for p-doped GaAs.

Within the investigated excitation limits, the polarization behavior of ZSGA mimics GaAs.

V. CONCLUSIONS

We conclude that there was no luminescence detected from the ZGSA layer. The spectral characteristics and polarization values are only understandable for GaAs. Even though we did not see any luminescence from the ZGSA layer, we were able to verify its presence by the dramatic effect the layer had on the luminescence from the substrate. As a consequence of the absorption behavior, we were able to approximate the type and energy position of the bandgap to be indirect and around 1.55 eV at 10 K, which also explained why we could not observe luminescence from the layer. An indirect bandgap, due to the phonon-assisted process necessary, is not an efficient source for luminescence. For the same reason, ZGSA is not suitable as a polarized electron source.

ACKNOWLEDGEMENTS

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Table 1. An estimate of the bandgap of $ZnGe_{0.68}Si_{0.32}As_2$ by linear interpolation at room temperature.

Compound	Bandgap (eV)	Type	Crystal Field Splitting (MeV)
$ZnSiAs_2$	2.12	pseudodirect	100
$ZnGeAs_2$	1.15	direct	40
$ZnGe_{0.68}Si_{0.32}As_2$	1.46	?	60

Table 2. A summary of the peak data for samples 5 (GaAs), 9 (ZGSA) and 13 (GaAs substrate of sample 13).

T (K)	Sample	E_L (eV)	E_1 (eV)	F_1 (MeV)	I_1 (cts/s)	E_2 (eV)	F_1 (MeV)	I_2 (cts/s)
10	5	1.66	1.47	26	800	1.50		250
		1.96	1.47	26	450	1.50	20	126
	9	1.66	1.475	30	93	1.50	22	21
		1.96	1.474	26	1	1.50	20	0.3
	13	1.66	1.470	27	1100	1.50	21	335
		1.96	1.470	27	644	1.50	20	180
100	5	1.96	1.47	38	100			
	9	1.96	1.47	35	0.7			

FIGURE CAPTIONS

Figure 1 A comparison of the emission spectra for samples 9 and 13 (10 K, HeNe).

Figure 2 The ZGSA absorption as a function of the excitation energy (100 K).

Figure 3 A comparison of the peak position of samples 9 and 13 as a function of the temperature (1.83 eV).

Figure 4 The luminescence polarization for samples 9 and 13 as a function of the excitation energy (10 K).

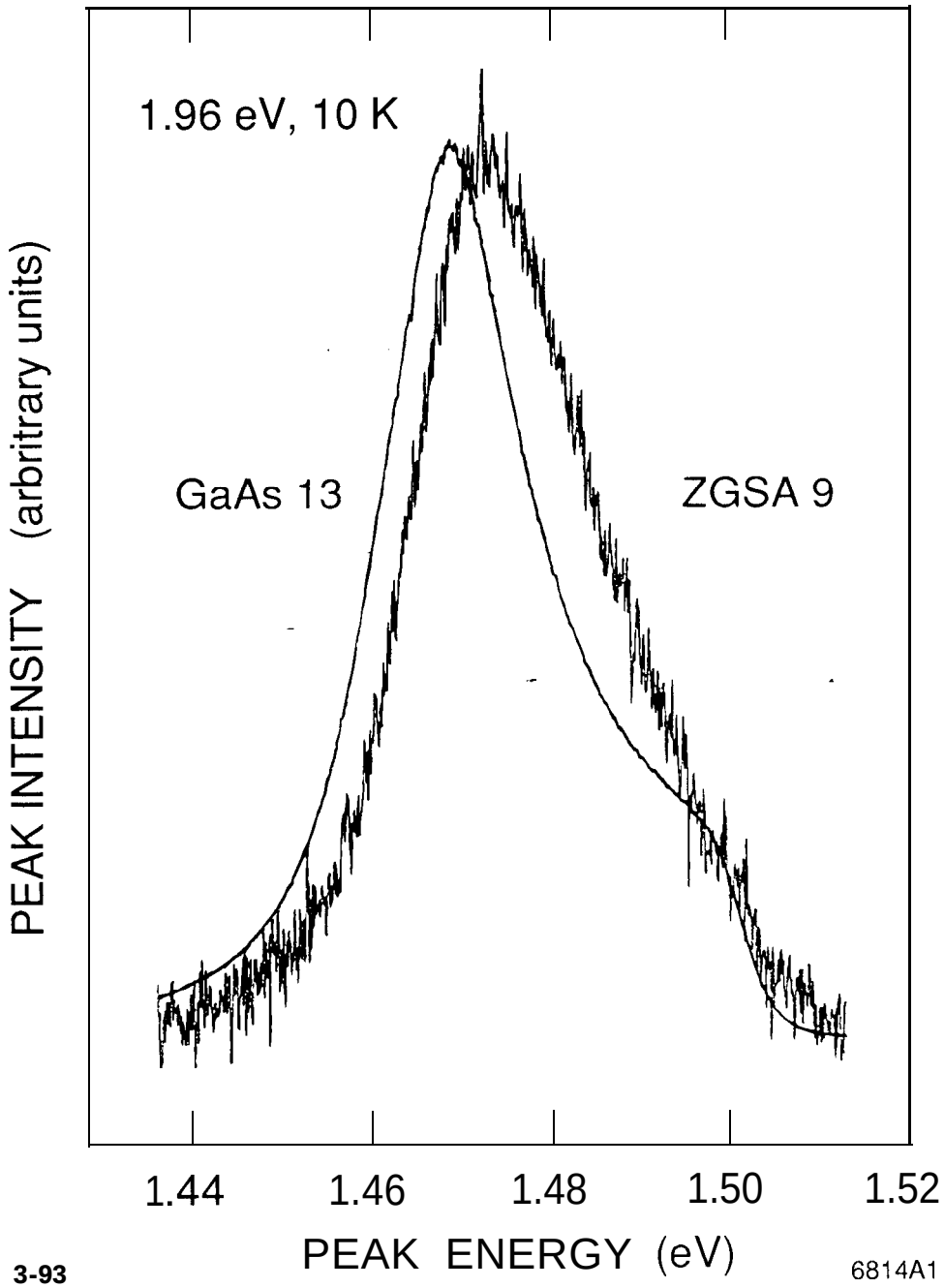
1.96 eV, 10 K
GaAs 13
ZGSA 9
PEAK INTENSITY (arbitrary units)
1.44
1.46
1.48
1.50
1.52
PEAK ENERGY (eV)
3-93
6814A1

Fig. 1

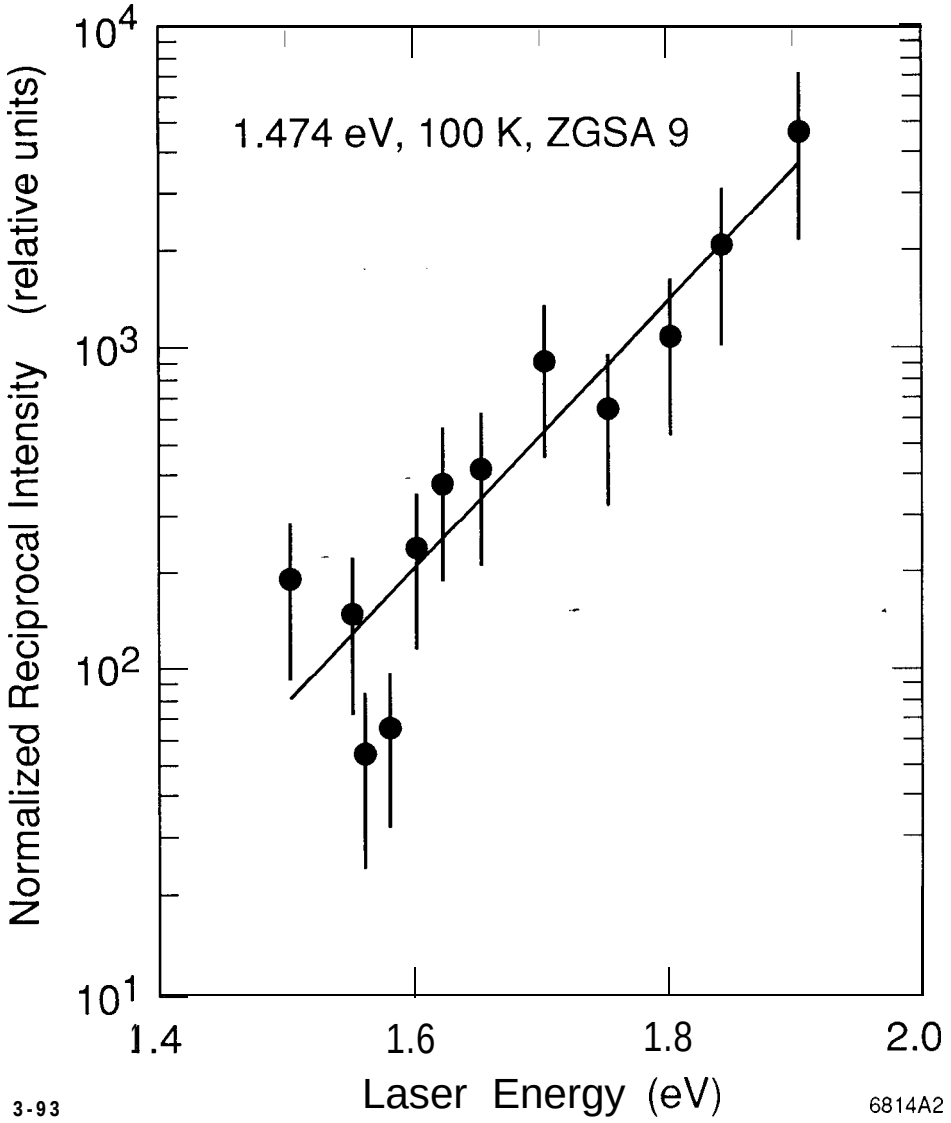
1.474 eV, 100 K, ZGSA 9
Normalized Reciprocal Intensity (relative units)
10^4
10^3
10^2
10^1
1.4
1.6
1.8
2.0
Laser Energy (eV)
3-93
6814A2

Fig. 2

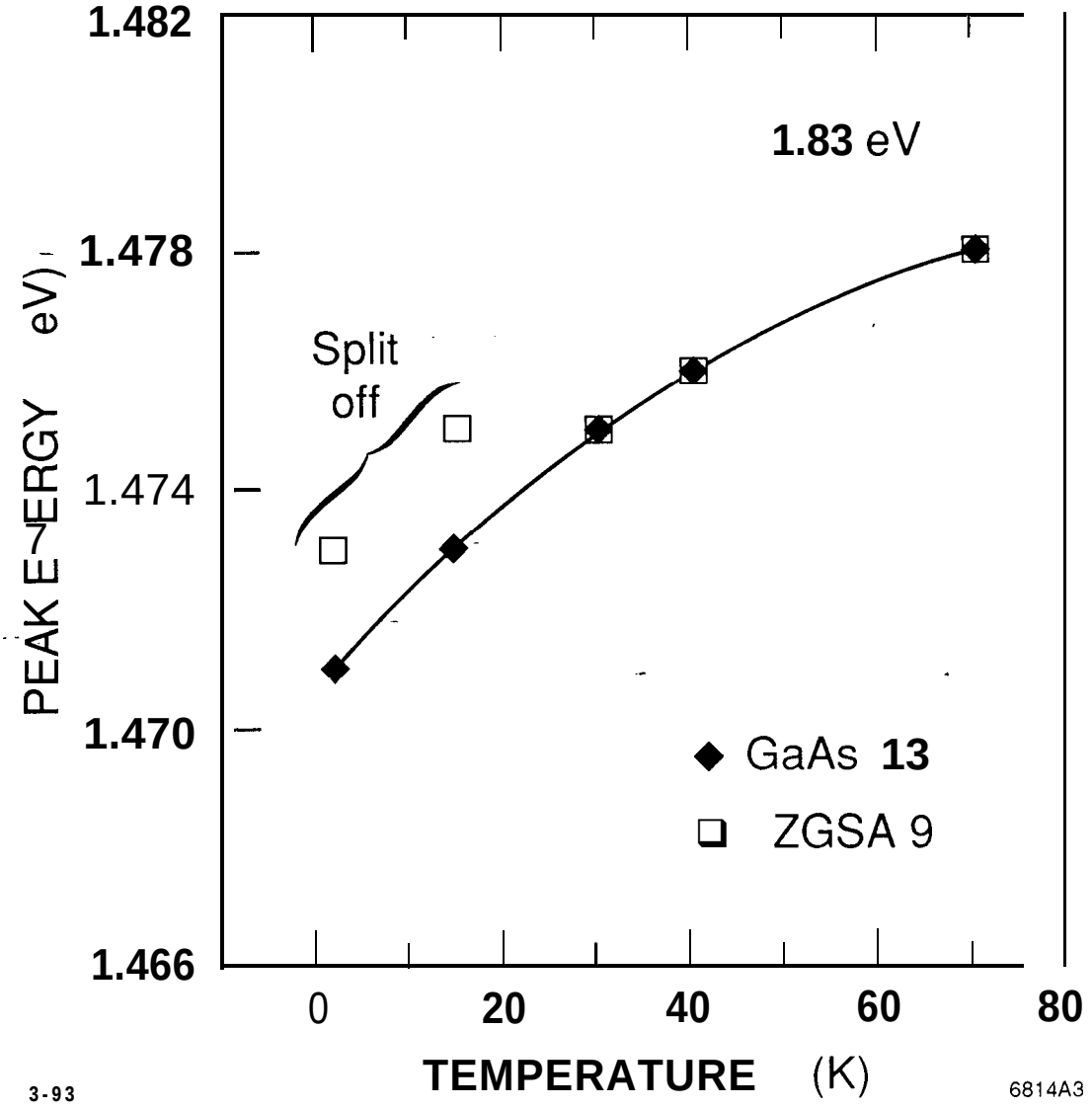
1.482
1.478
1.474
1.470
1.466
PEAK E~ERGY eV)
1.83 eV
Split
off
GaAs 13
ZGSA 9
0
20
40
60
80
TEMPERATURE (K)
3-93
6814A3

Fig. 3

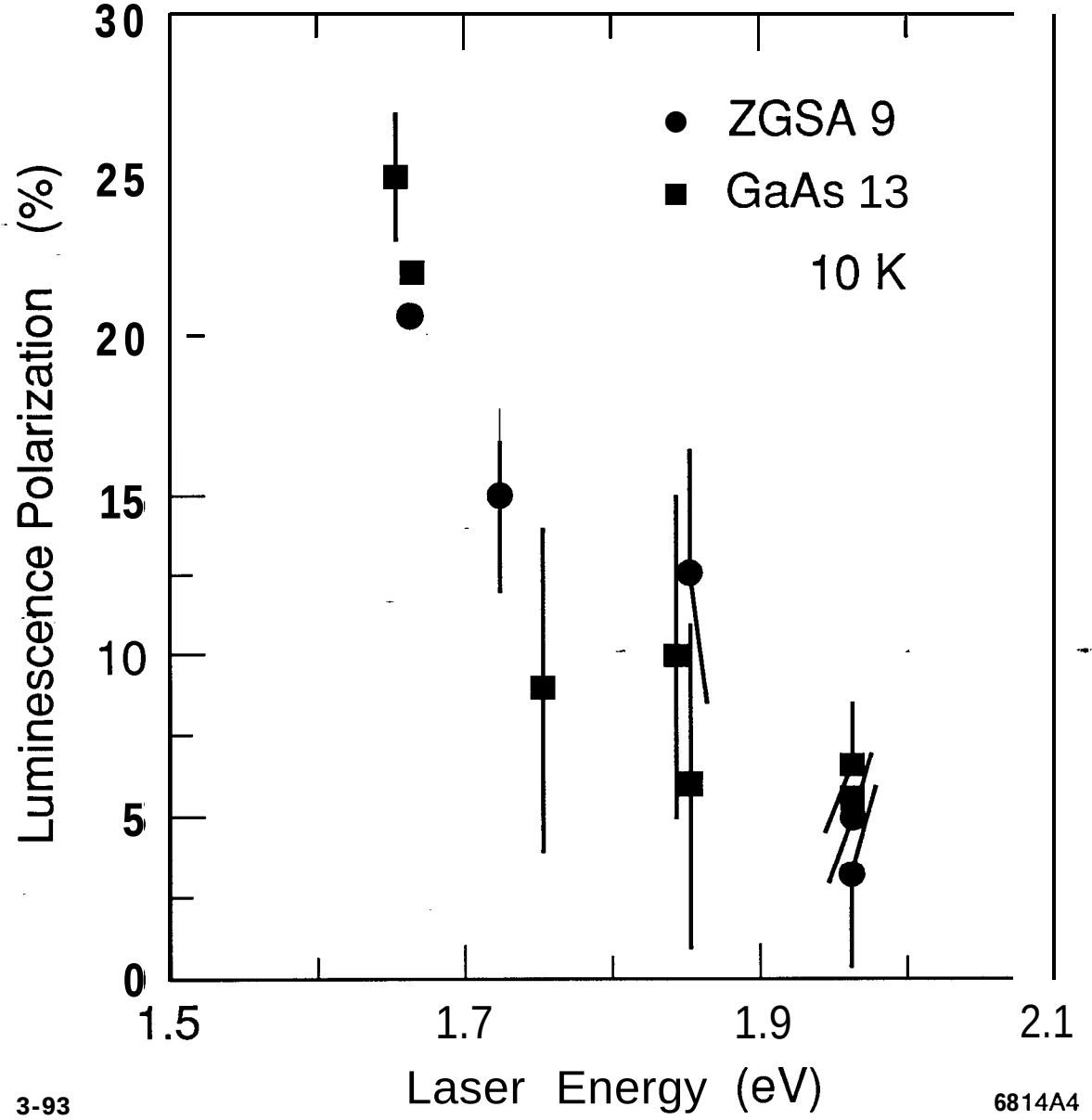
30
25
20
15
10
5
0
Luminescence Polarization (%)
ZGSA 9
GaAs 13
10 K
1.5
1.7
1.9
2.1
Laser Energy (eV)
3-93
6814A4

Fig. 4