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Optical and spin properties of localized and free excitons in $GaBi_xAs_{1-x}$ /GaAs multiple quantum wells

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Raman Spectroscopy and magneto-photoluminescence measurements under high magnetic fields were used to investigate optical and spin properties of GaBiAs/GaAs multiple quantum wells (MQWs). An anomalous negative diamagnetic shift was observed at higher temperatures and higher laser intensities and was associated to a sign inversion of hole effective mass in these structures. In addition, it was observed an enhancement of polarization degree with decreasing of laser intensity (experimental condition where the emission is dominated by localized excitons). This effect was explained by an increase of spin relaxation times due to exciton localization by disorder.

I.INTRODUCTION

III- V dilute bismide semiconductor material has attracted much attention in recent years due to its potential applications for near infrared wavelength photonics and spintronics [1-20]. The incorporation of Bi has been shown to have a dramatic impact on the band structure of GaAs. A band gap reduction of around 90 meV per percent of Bi and a large increase of spin-orbit (SO) split-off energy have been observed [1-20]. This increase of spin-orbit interaction could suppress the non-radiative Auger recombination processes that affect the efficiency of lasers in the near infrared; it is also very attractive for semiconductor spintronics. On the other hand, GaBiAs alloys have important disorder effects mainly due to potential fluctuations associated to Bi composition variation and the formation of clusters [18-20]. These disorder effects have significant impacts on the optical emission of this material. Therefore, the investigation of disorder effects is an important issue for bismide alloys in photonics and spintronics; particularly for GaBiAs/GaAs quantum wells (QWs), which are important for further development of GaBiAs based devices.

Recently, much attention has been paid to the spin properties of GaBiAs alloys. A decrease of spin relaxation times was observed for GaBiAs alloys and associated to the increase of spin-orbit (SO) split-off energy. It was also reported that the *g-factor* of GaBiAs is highly anisotropic and that its value increases strongly with the increasing Bi composition [18]. These spin properties were theoretically explained by an important increase of spin-orbit-splitting energy and hybridization of the extended states of the

GaAs valence band edge with localized Bi-related states in disordered $GaBi_xAs_{1-x}$ alloys [18].

In this paper, we have investigated the effect of disorder on the optical and spin properties of GaBiAs/GaAs multiple quantum wells (MQWs). We have observed an anomalous negative diamagnetic shift at higher temperatures and higher laser intensities (experimental conditions under which the emission is dominated by free excitons). This result evidences negative values of hole effective mass in these materials. An enhancement of polarization degree at lower energies (experimental conditions under which the emission is dominated by localized excitons) with decreasing laser intensity was also observed. This effect was explained by an increasing of spin relaxation times, due to the localization of excitons by alloy inhomogeneities and clusters. It was also observed that the excitonic g-factor increases with increasing Bi concentration as expected by previous theoretical investigations [18].

II- EXPERIMENTAL DETAILS

Our samples consist of $GaAs_{1-x}Bi_x$ /GaAs multiple quantum wells (MWQs) grown by solid-source molecular beam epitaxy (MBE) on semi-insulating undoped GaAs (001) substrates. The growth temperatures were set in the range 385–415 °C depending on the desired Bi concentration. Details of the growth and determination of Bi concentration can be found in references 9-10. Raman measurements were performed with a triple grating spectrometer, using the 514 nm line of an Argon laser as the excitation source. Polarization resolved photoluminescence (PL) measurements were performed in an

Oxford Magnet with optical window and magnetic fields up to 15T in Faraday configuration (magnetic field parallel to the growth direction), using a linearly-polarized 532 nm laser line for optical excitation. As a consequence, the photogenerated carriers in the GaBiAs MQWs do not have any preferential spin polarization. At this condition, the polarization degree is due to a simple thermal occupation of the QW spin-splitting levels under the magnetic field. The PL measurements were performed by using a 0.5 m Spex monochromator and a nitrogen cooled Ge detector. Right (σ^+) and left (σ^-) circularly-polarized photoluminescence signals were selected with appropriate optical components.

III. RESULTS AND DISCUSSION

Figure 1 (a) shows the Raman spectra of GaBiAs/GaAs MQWs for different Bi concentration (1% and 4.9%) at room temperature. The most prominent peak at 291cm^{-1} is attributed to the longitudinal optical phonons of GaAs (LO_{GaAs}). On the other hand, the peak observed at 271cm^{-1} is attributed to transverse optical phonons (TO_{GaAs}), despite its occurrence being forbidden by the Raman selection rules in the backscattering geometry. In this configuration, observation of the TO_{GaAs} peak can only be activated by disorder effects. Furthermore, we have observed that as the Bi concentration is increased, the TO_{GaAs} peak becomes more intense, indicating that the increase of Bi% concentration leads to an increase in the structural disorder. This effect can also be evidenced by measuring the light scattering with specific polarization geometries. Figure 1 (b) shows Raman spectra taken in polarization configurations z(x,y)-z and z(y,y)-z, where z=[001] and –z=[00-1] represent the direction of incident and scattered photons, respectively, and x=[110] and y=[1-10] are their polarizations relative to crystal planes of samples. According to the Raman selection rules for crystals for zinc-blend structures, the LO peak is allowed in –z(y,y)z geometry and forbidden in z(x,y)-z. However, in our measurements the relative intensity of LO peak is not suppressed in the z(x,y)-z spectrum. This selection rule breakdown is attributed to an important structural disorder induced by bismuth insertion in the MQW lattices.

A previous study of PL versus laser power and temperature was performed for these samples which evidenced strong localization effects by defects in the GaBiAs MQWs [10]. Particularly, it was reported that the PL spectra showed two bands separated by about 100meV which are due to localized and free excitons [10] (please also see PL spectra in Figure 3). In addition, under low temperatures and low laser intensity it was evidenced that the PL is dominated by excitons localized by defects. However, under higher temperatures (T > 150K) and laser power it was observed that PL is dominated by free excitons. For this reason, we have chosen to perform magneto PL measurements for the experimental conditions where one of the two peaks dominates. Figure 2 shows the magnetic shift as function of magnetic field for these two experimental conditions: (a) at low temperature and low laser intensity (PL dominated by localized excitons) (b) high temperatures and high laser intensity (PL dominated by free excitons). For both experimental conditions, it was observed that the magnetic shift is very small (about 5 meV at 15T) which evidences important localization of excitons due to disorder effects, even for the condition where the PL is dominated by free excitons. It has been previously reported that this localization of carriers is mainly due to composition variation and cluster formation [3, 4]. In addition, an anomalous negative magnetic shift as function of magnetic field was observed for higher temperatures (Figure 2(b)), which evidences important changes in the excitonic reduced mass. Particularly, this result can only be explained for a negative effective mass of the valence band ground state in GaBiAs QWs. Similar results were observed previously for InGaAsN/GaAs QWs in the literature and theoretically described by changes in reduced mass due to the strain and confinement modulation in dilute nitrides [24]. Actually, it is expected that important changes in the valence band can occur with the introduction of Bi, including the band valence effects investigated in this previous paper [24].

Figures 3 and 4 show typical $\sigma+$ and $\sigma-$ polarization resolved PL spectra for the 1% and 4.9% Bi samples at 2K and under 0 and 15T for different laser power conditions by using linearly polarized laser excitation. As mentioned before under these conditions, the polarization degree is due to a simple thermal occupation of the QW spin-splitting levels under the magnetic field. Figure 5 shows the PL spectra and the energy dependence of the circular polarization degree under 15T. We remark that the optical emission is $\sigma-$ polarized. We have also estimated the polarization degree as function of energy (Fig.5). It was observed that the polarization degree is higher at lower energies which are usually associated to emission from excitons localized by disorder (Fig.5). It was also observed that the total polarization degree increases with decreasing laser power for all samples (Figures 6 and 7). This effect is more important for the sample with higher Bi% concentration (Figure 7) which has incorporated more defects and has shown an increase of structural disorder in Raman results (Figure 1). It is well known that localization effects in PL spectra are particularly important at lower temperatures. As mentioned previously, under these conditions, the radiative recombination in GaBiAs/GaAs QWs is dominated by localized excitons. Besides alloy inhomogeneities (fluctuation of Bi concentration and clustering of Bi atoms) and point defects are responsible for emission of localized excitons. Our magneto-PL results show that the localization of carriers by defects contributes considerably to the increase of spin polarization degree in the GaBiAs QWs. Actually, it is well known that localization effects can increase the spin lifetimes of holes and electrons in semiconductors [22-23]. Long spin relaxation times were reported for GaInNAs/GaAs QWs and were explained by the localization of excitons due to nonradiative deep centers [20]. Similar effects can consequently enhance the spin polarization in GaBiAs QWs and therefore explain our experimental results.

The spin polarization degree of carriers in the QW was calculated by using the relation: $P = (I^{\sigma+} - I^{\sigma-}) / (I^{\sigma+} + I^{\sigma-})$, where $I^{\sigma+}$ and $I^{\sigma-}$ are the total integrated PL intensities of the right and left circularly-polarized emissions. We have also calculated the excitonic spin splitting by the energy peak difference of the $\sigma+$ and $\sigma-$ emissions. Figures 6 and 7 display the magnetic field dependence of the circular polarization degree and excitonic spin-splitting for both samples and both experimental conditions (low and high laser power conditions). We remark that the polarization degree increases almost linearly with magnetic field. In addition, the difference of polarization degree between the two experimental conditions is enhanced for the 4.9% Bi% sample. This effect can be explained by the expected increase of disorder as we increase the Bi% which is responsible for localization of excitons. As mentioned before it is well known that the localization of carriers can increase their spin relaxation times and consequently the spin polarization degree in these samples. It was also observed that the spin splitting increases with increasing Bi%, which is expected from previous theoretical calculations for GaBiAs layers. In addition, We have estimated excitonic g-factors under higher laser power at 15T in order to reduce the contribution of localized excitons for those samples; we have obtained higher g_{ex} factors (~3 for 1% and 5 for 4.9% Bi) than the values previously obtained for GaAs (~1) [14].

IV. CONCLUSION

In conclusion, we have observed an increase of g-factors and polarization degree with the increasing Bi%. We report a higher g_{ex} factor (~3 for 1% and 5 for 4.9% Bi) than that of GaAs-GaAlAs QWs. These results are attributed to confinement and important Bi-related changes in the hole band structure of GaBiAs. An important increase of polarization degree with decreasing laser power was also observed. This enhancement of polarization degree was attributed to an increase of spin relaxation times due to localization of excitons by defects. An anomalous negative diamagnetic shift was also observed at higher temperatures and higher laser intensities which evidences sign inversion of the hole effective mass in these structures. However, further theoretical studies for GaBiAs structures are needed in order to explain this anomalous behavior for the magnetic shift.

ACKNOWLEDGMENTS

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Figure Captions:

Figure 1(a). Room temperature Raman Spectra of GaBiAs/GaAs MQWs with Bi concentration 4.9% and 1%.The peak assigned with an asterisk is a plasma emission line from the argon-ion laser. b) Raman spectra of MQWs with 4.9% of Bi in z(y,y)-z and z(x,y)-z scattering geometries

Figure 2(a). Diamagnetic shift as function of magnetic field at lower temperatures (2K) and lower laser power (0.2mW) (condition where the emission is dominated by localized excitons) (b) Diamagnetic shift as function of magnetic field at higher temperatures (165K) and higher laser power (20mW) (condition where the emission is dominated by free excitons). The inserts show details of the PL spectra at 0 and 14T .

Figure 3. Polarization resolved PL spectra for 0T and 15T for 1% Bi sample for lower and higher laser power excitation at 2K.

Figure 4. Polarization resolved PL spectra for 0T and 15T for 4.9% Bi sample for lower and higher laser power excitation at 2K.

Figure 5. Polarization resolved PL spectra and polarization degree for the 4.9% Bi sample for lower (a) and higher laser power excitation (b) and under 15T at 2K.

Figure 6. Magnetic field dependence of polarization degree and spin splitting for the 1% Bi QW at 2K.

Figure 7. Magnetic field dependence of polarization degree and spin splitting for the 4.9% Bi sample at 2K.

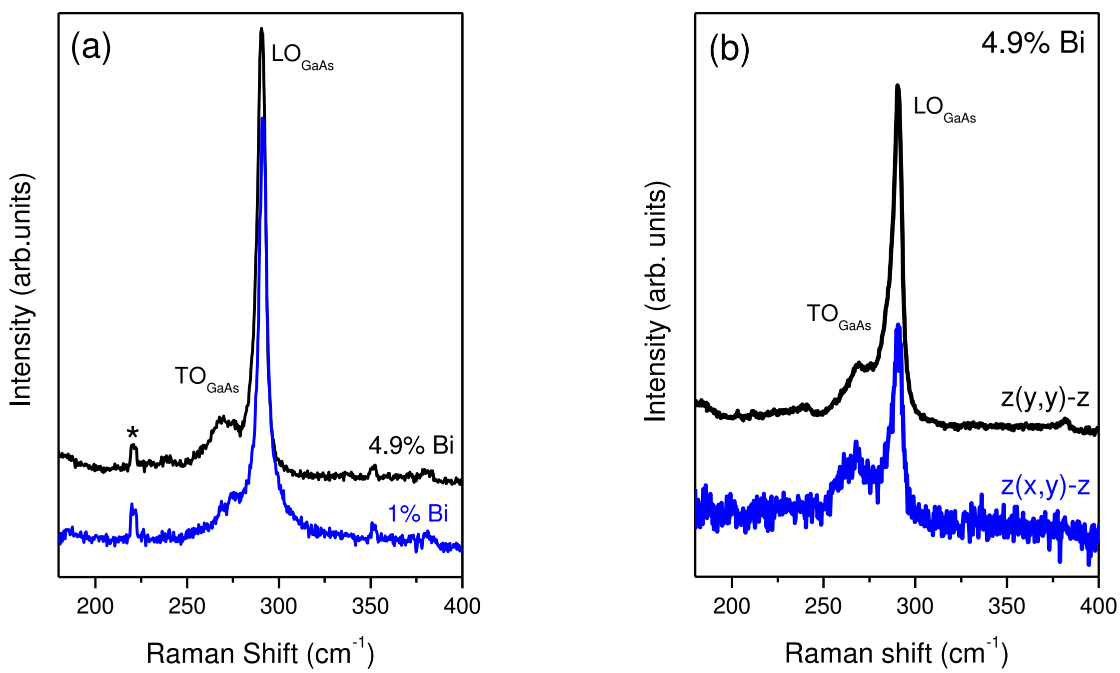
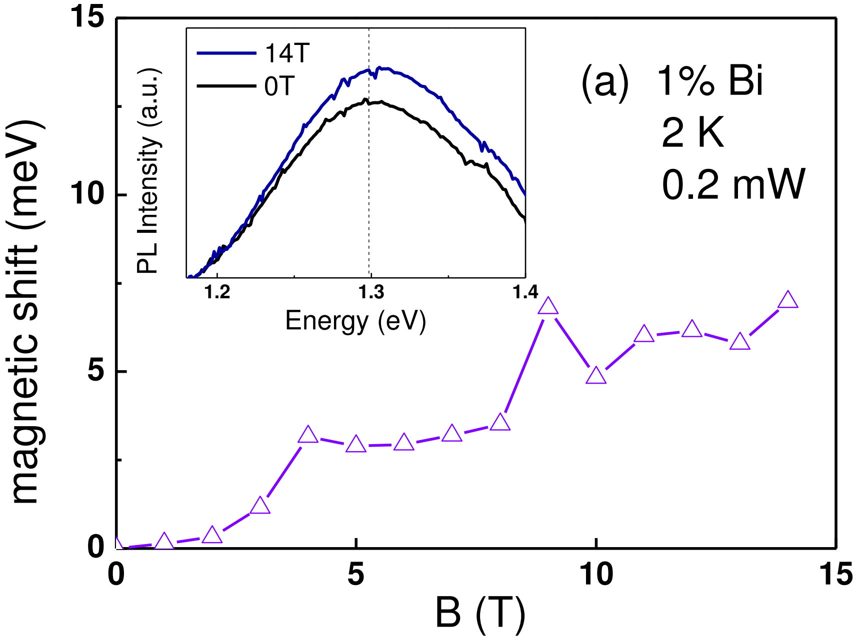

(a)
LO$_{GaAs}$
TO$_{GaAs}$
*
4.9% Bi
1% Bi
Intensity (arb.units)
200
250
300
350
400
Raman Shift (cm^{-1})
(b)
4.9% Bi
LO$_{GaAs}$
TO$_{GaAs}$
z(y,y)-z
z(x,y)-z
Intensity (arb. units)
200
250
300
350
400
Raman shift (cm^{-1})

Figure 1.


(a) 1% Bi
2 K
0.2 mW
14T
0T
PL Intensity (a.u.)
Energy (eV)
magnetic shift (meV)
B (T)

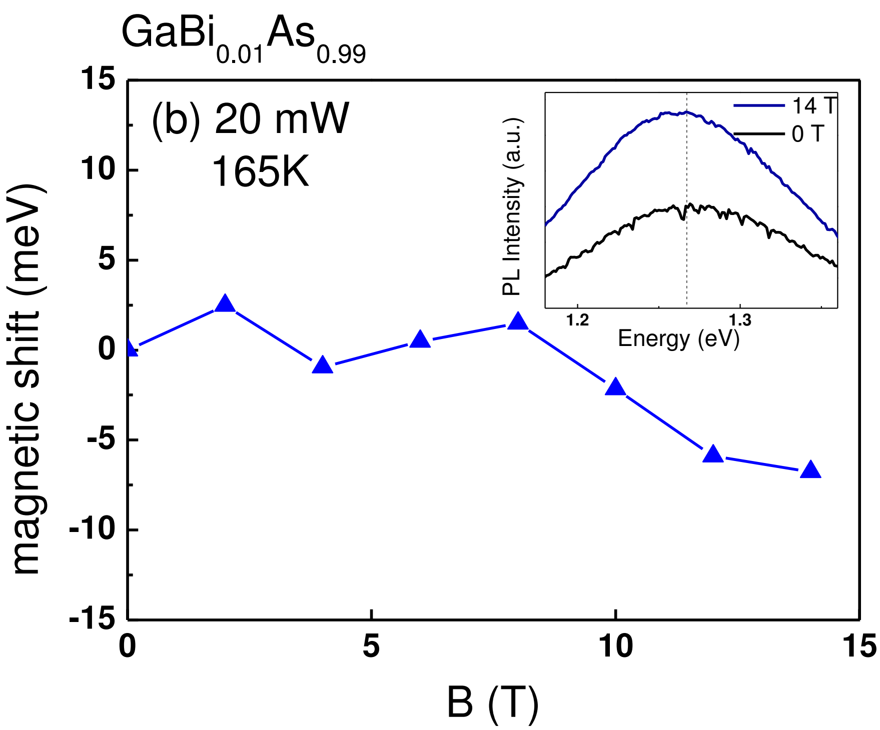

GaBi0.01As0.99
(b) 20 mW
165K
14 T
0 T
PL Intensity (a.u.)
Energy (eV)
magnetic shift (meV)
B (T)

Figure 2.

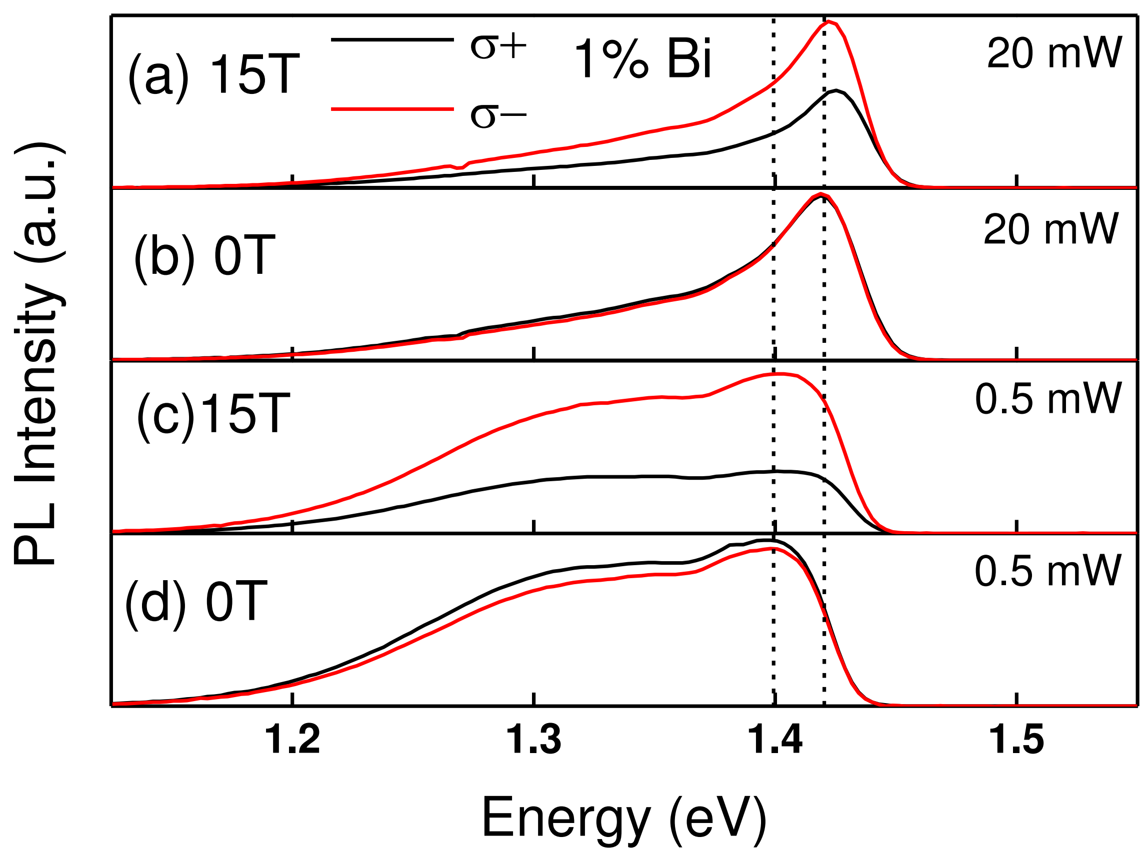

(a) 15T
σ+
σ−
1% Bi
20 mW
(b) 0T
20 mW
(c)15T
0.5 mW
(d) 0T
0.5 mW
PL Intensity (a.u.)
1.2
1.3
1.4
1.5
Energy (eV)

Figure 3.

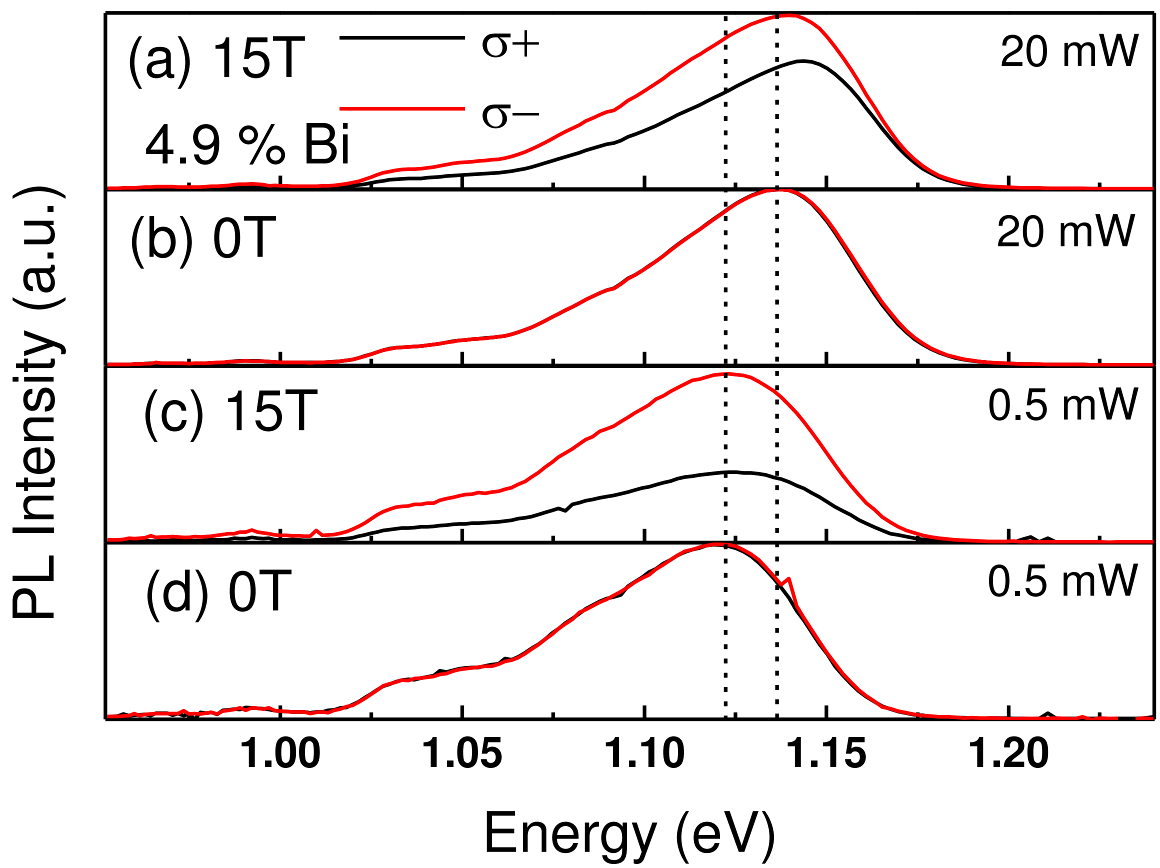

(a) 15T
σ+
σ−
4.9 % Bi
20 mW
(b) 0T
20 mW
(c) 15T
0.5 mW
(d) 0T
0.5 mW
PL Intensity (a.u.)
1.00
1.05
1.10
1.15
1.20
Energy (eV)

Figure 4.

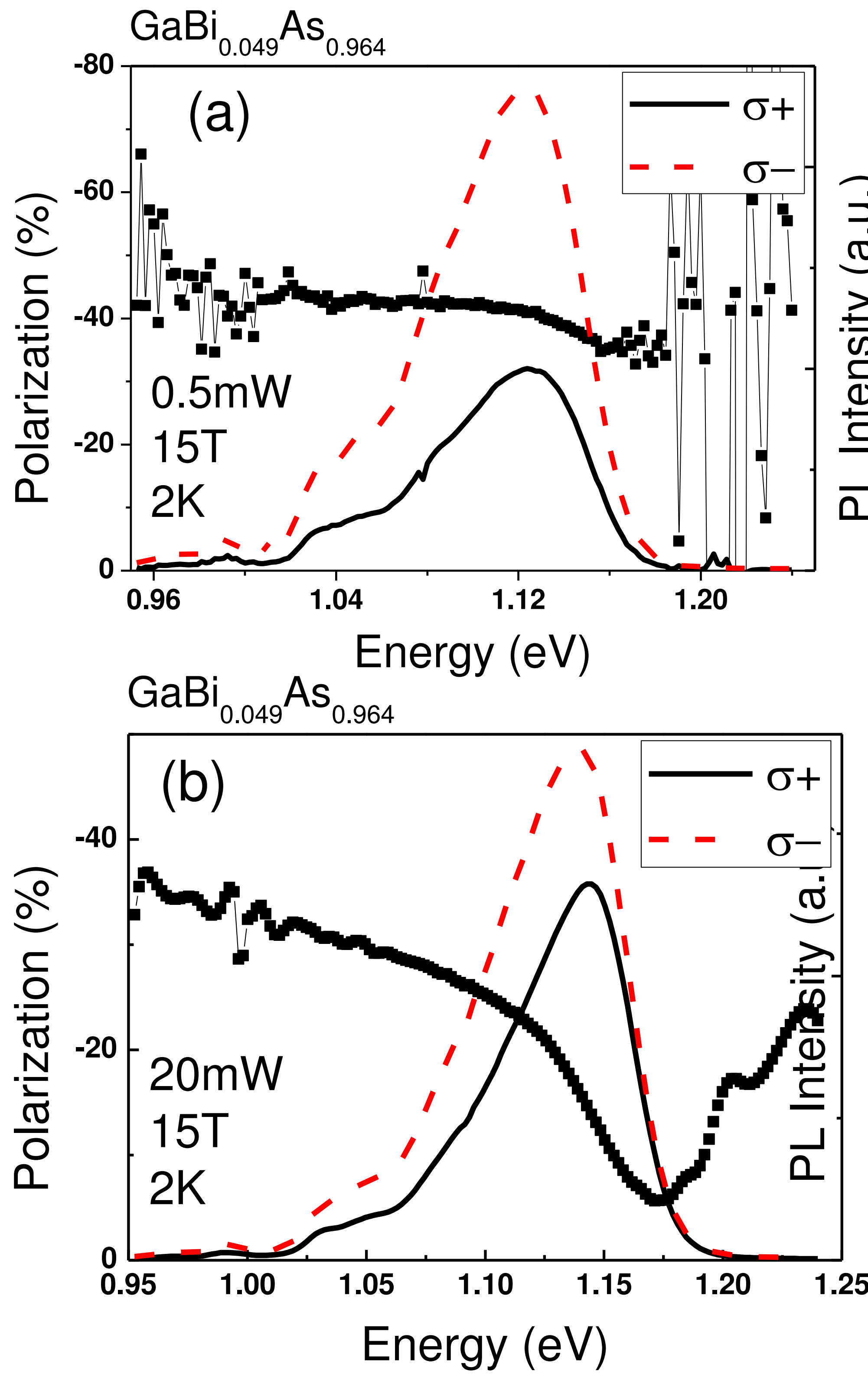

GaBi0.049As0.964
(a)
σ+
σ−
0.5mW
15T
2K
Polarization (%)
PL Intensity (a.u.)
Energy (eV)
GaBi0.049As0.964
(b)
σ+
σ−
20mW
15T
2K
Polarization (%)
PL Intensity (a.
Energy (eV)

Figure 5.

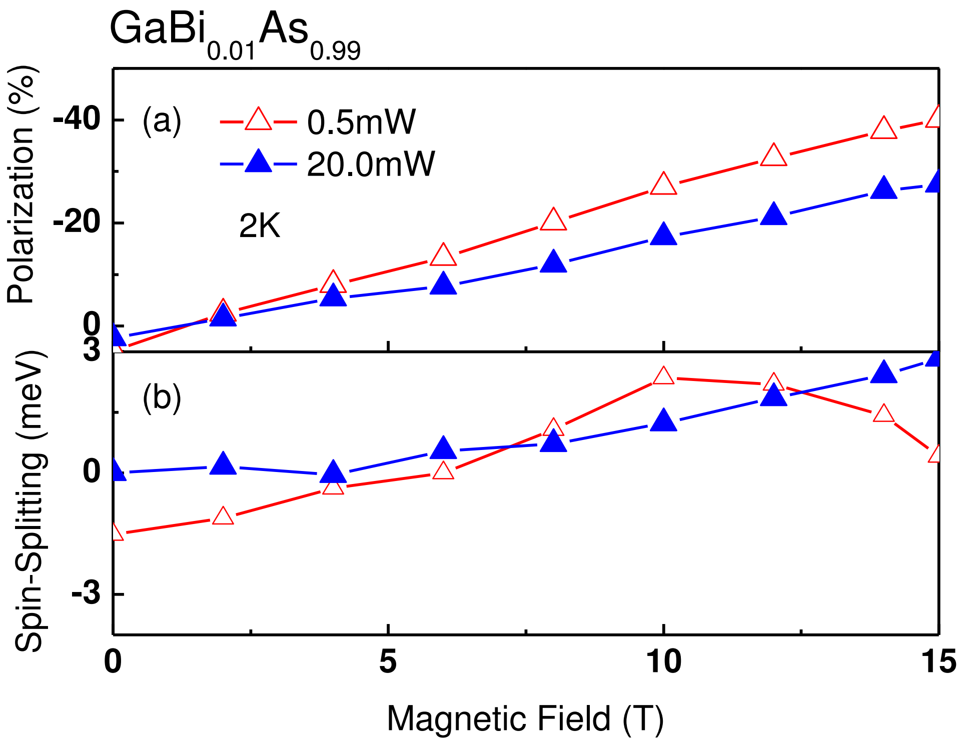

GaBi0.01As0.99
Polarization (%)
-40
-20
0
(a)
0.5mW
20.0mW
2K
3
(b)
Spin-Splitting (meV)
0
-3
0
5
10
15
Magnetic Field (T)

Figure 6.

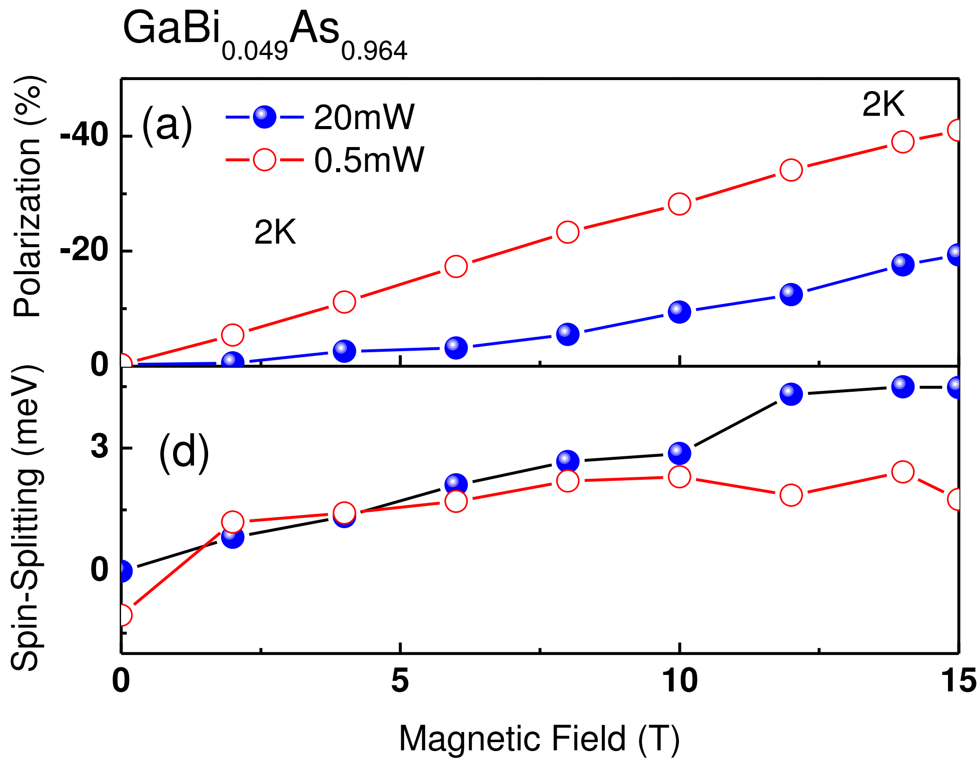

GaBi0.049As0.964
(a)
20mW
0.5mW
2K
2K
Polarization (%)
-40
-20
0
(d)
Spin-Splitting (meV)
3
0
0
5
10
15
Magnetic Field (T)

Figure 7.