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New Light Modulator Using GaSe Layered Crystal

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Layered crystals GaSe are grown by Bridgman method. Transmission spectra are measured for various sample configurations with respect to c-axis, applied electric field, direction of light incident and polarization. Absorption edge shifts toward longer wavelength by 20 nm under an electric field of 1 kV/cm, which shift is two orders larger than evaluated on the Franz-Keldysh mechanism. Switching time is estimated to be 53 ns or less.

§.1 Introduction

There have been many reports[1-4] on the characteristics of GaSe relating to its layered structure, which consists of stacks of four layer sheets of the sequence -Se-Ga-Ga-Se-. Mooser *et al.* reported on an exciton near the fundamental band edge absorption of GaSe[1]. Abdullayeva *et al.* reported on electro-absorption spectra of $GaSe_xS_{1-x}$ in the fundamental absorption edge and referred to existence of various phases of layered structures[2].

The layered structure can be regarded as a pseudo superlattice, because it is formed by stacking the four layer sheets on the c-plane and it is expected to exhibit interesting properties, characteristic of the superlattice. There have, however, been no report investigating the layered semiconductors from this view point.

We have focused on the absorption edge shift of the layered GaSe crystal by electric field and reported[5], for the first time, that the absorption edge of GaSe is two orders more sensitive to the applied electric field than any other semiconductor materials ever reported.

The main purpose of this report is to describe the configuration dependence of the absorption edge shift of the layered GaSe crystal by electric field and switching characteristics and propose a device in which 100 % intensity modulation of a light from a He-Ne laser is made possible by a new GaSe device drived directly with a transistor.

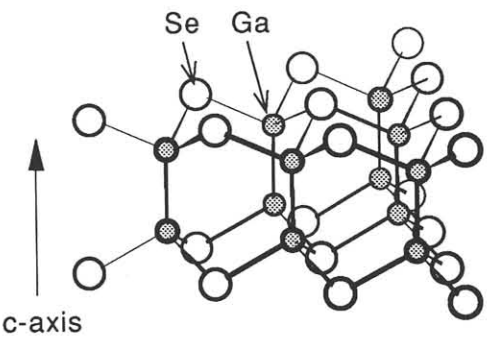

Fig.1 Schematic diagram of the structure of GaSe layered crystal.

§.2 Experimental Procedures

Crystals of GaSe were grown by Bridgman method from stoichiometric amounts of 6-N Ga and Se. Crystals obtained

were hexagonal β-GaSe[1] (S.G.=D^4_{6h}, layered crystal, cleavable in a c-plane). It had resistivity of 1.3 x 10^4 Ω cm in dark.

Several types of samples with different configurations were prepared as shown in Fig.2 and Fig.3 , various combinations of the c-axis, the electric field and the incidence and polarization direction of light. Thin Au electrodes with around 40 % transmission were vacuum deposited on both sides of the sample for longitudinal electric field (type A in Fig.2) and In electrodes were used for transverse electric field (type B and C in Fig.3).

DC voltage up to 90 V for the type-A or pulse voltage up to 900 V for the type-B and C was applied to the sample, which corresponded to an electric field of 6000 V/cm. All measurements were done at room temperature. Transmission spectrum was obtained using polarized light under the applied field.

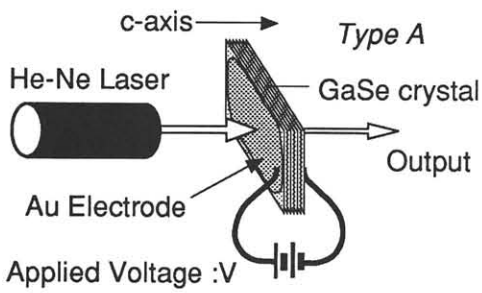

Fig.2 Experimental configuration and type A sample.

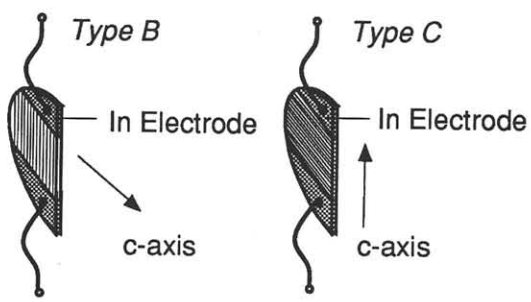

Fig.3 Type B and C samples with different direction of c-axis and electric field.

In order to obtain switching characteristics, polarized light from the He-Ne laser was incident normal to the surface of the samples, the output light was detected by a PIN diode and the switching time was figured out using a digital oscilloscope.

§.3 Experimental Results

Figure 4 shows typical transmission spectra of the type A sample under the various applied voltages. The absorption edge without applied voltage was 623 nm (1.99 eV) and agrees fairly well with the energy gap reported 2.036 eV[1]. The absorption edge moves toward longer wavelength as the applied voltage increases. Large shift of the absorption edge around 20 nm, which corresponds to 63 meV, was observed by applying 20 V, which corresponds to the field of 1250 V/cm.

Similar transmission spectra for the type-B and C were obtained. Their absorption edge shifted considerably by the applied field similar to the case of the type A.

As the absorption edge moves to longer wavelength than 632.8 nm by applying 20 V to

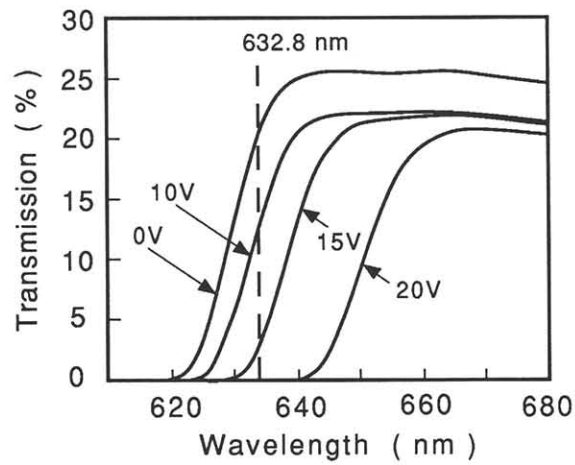

Fig.4 Transmission spectra for type A sample, under applied voltage of 0, 10, 15 and 20V. Thickness of the sample is 0.16mm[5].

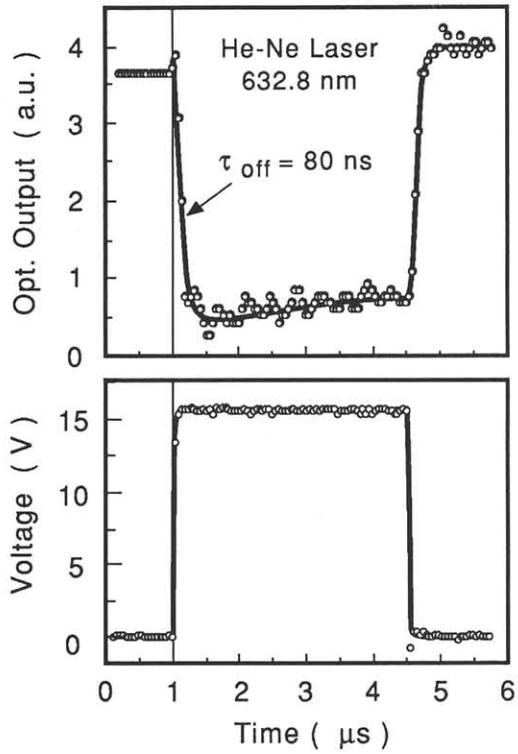

Fig.5 Typical switching wave form of optical output (above) for type A sample and applied pulse voltage (below).

the type A in Fig.4, this device may act as light modulator for He-Ne laser (λ = 632.8 nm) so that the output light is turned off in applying 20 V.

Switching wave form is shown in Fig.5 together with the applied pulse voltage. Actual switching time is estimated to be 53 ns or less, because a response time of the PIN diode detector is about 60 ns.

The shift of the absorption edge $\Delta\lambda$ is the difference between the absorption edges with and without applied field. Relations between $\Delta\lambda$ and the applied field E are shown in Fig.6 for various types of the samples. The $\Delta\lambda$ varies as $E^{2.0}$ for configuration A, B and C in Fig.6 in which plane of polarization Pis parallel to c-axis . And it varies as $E^{2.3}$ for configuration B' and C' in which P is perpendicular to c-axis.

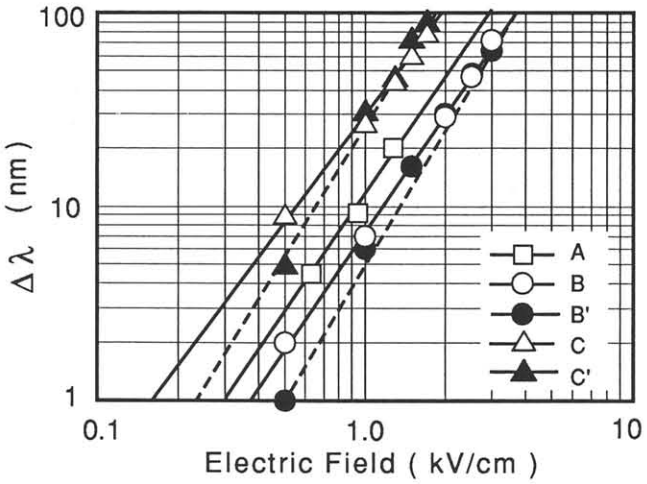

Fig.6 Dependence of the shift of absorption edge $\Delta\lambda$ on electric field for various configurations.
A : type A, independent of P.
B : type B, P perpendicular to c-axis.
B ' : type B, P parallel to c-axis.
C : type C, P perpendicular to c-axis.
C' : type C, P parallel to c-axis.
where P is plane of polarization.

§ 4 Discussion and Conclusion

Shift of the absorption edge of GaSe layered crystal described in this report is anomalously large compared to any other semiconductor materials ever-reported. The band edge shift evaluated from the Franz-Keldysh theory is only 0.74 meV under the applied electric field of 1.0 kV/cm. Our result in the type A sample, for example, is 25 meV under the same applied electric field. These figures indicate our effect is a factor of 34 larger than the standard Franz-Keldysh effect. It should therefore be impossible to explain the effect by the standard theory.

A possible model of the large band gap change is as follows. It would surely be related with the layered structure of the GaSe crystal. The layered structure may be viewed as a natural superlattice with a period of 4 atomic layer sheet. The lowest electronic state of the superlattice is very sensitive to the fundamental period or the relative change of the

spacings between monoatomic layers.

The binding strength between the 4 layer unit sheets are relatively weak in such a layered structure. The spacing between the unit sheets may be changed by the applied electric field. Even a small change in the spacing would effect a relatively large change of the band gap energy. The change of the relative positions of the constituent ions would be necessary to explain such a large effect.

An important aspect to be noted is configurational dependence of the effect. Though there are some difference in this effect among the different configurations up to a factor of ten, the effect is much larger, in any configuration, than expected from the theory. The configuration A and the configuration C is the same in the direction of the electric field and the polarization relative to the crystal orientation. There are, however, the factor of three difference in its effect between these two configurations. The structural difference between the two configurations is: contact metals, indium and gold and the incidence direction. The incidence direction would not affect the band gap energy and the contact metal is a more plausible cause of the difference. While indium is expected to make ohmic contact to GaSe, gold may make Schottky contact to GaSe. This will make different field distribution in the crystal and different field effect. It is now under further investigation.

The direction of the electric field relative to the crystal orientation in the configuration B and B' is different from the other configurations. It is parallel to the c-plane or perpendicular to the c-axis. Even in this field direction, the effect is not so small, though there are factor of ten difference.

We have investigated the large band gap shrinkage effect in GaSe layered crystal due to applied electric field in several different configurations. The origin of the effect is not yet clear, but the effect must surely be related with the layered structure of the crystal and possibly with relative movement of the constituent ions.

The effect is anomalously large and it is large enough to apply it for modulation of light by using only a transistor driver without any polarizer. There are also possibility of changing the relevant wavelength range by making a mixed crystal[5].

The configuration A may be suitable for the light modulator because of ease of preparation and independence of plane of polarization.

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