PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 353–356

STARK LADDER RESONANCE IN ZnS*

N. Sawaki and T. Nishinaga

Department of Electronics
Nagoya University
Chikusa-ku, Nagoya 464
Japan

The dc photo-current of a hexagonal ZnS was studied at 100 - 300 K under a high electric field up to 300 kV/cm. An oscillation of the second derivatives of the current with respect to the field was found as a function of the field, which is attributed to the resonant interaction of electrons in the quantized Stark ladders with longitudinal optical phonons.

I. Introduction

Since Wannier[1] proposed the possibility of a discreat quantized level in solids under a high dc electric field (Stark ladder), many investigators have challenged to prove it. In spite of various theoretical and experimental efforts, there have never been a conclusive evidence of the effect.

Maekawa[2] and May and Vecht[3] studied the electrical conductivity of an evaporated thin film of ZnS, of which crystal structure was cubic, and found an oscillation of the conductivity due to the electron-phonon interaction in Stark ladders. But the presence of the large current component due to Poole-Frenkel effect as well as the absence of the current saturation due to hot electron effect in the lower field region did make the detailed examination of the results difficult[4].

In this paper, more convincing evidence of the Stark ladder is presented. In the course of a study of the high field transport of ZnS, an oscillation of the second derivatives of the photo-current with respect to the field was found as a function of the field, which is attributed to the hopping conduction in quantized Stark ladder levels via the electron-phonon interactions.

II. Experimental

An insulating ZnS single crystal (Eagle Picher Inc., hexagonal crystal of 10^{10} - 10^{12} Ω-cm) was cut along (0001) plane and lapped mechanically into wafers of thickness 30 - 300 µm. Indium and/or In_2O_3 were evaporated on both sides of the etched surfaces to form semi-transparent ohmic electrodes of radius 1.5 - 2.0 mm. The sample was placed on a liq.N_2 cold finger and the electrical conduction was studied at 100 - 300 K in a vaccum of 10^{-3} Torr. By shining light of Hg lamp through an appropriate glass filter, photo-electrons were excited uniformly in the sample.

III. Experimental Results and Discussion

The current in the dark was temperature sensitive and was due to Poole-Frenkel effect, and there was no increase of the current by the avalanche breakdown or by the injection from the electrodes. The dc photo-current vs field characteristics was ohmic at low fields and a current saturation due to hot electron effect was set on at $E \geq 3$ kV/cm. A typical example is shown in Fig.(1). The conductivity at the ohmic region is $\sim 5\times10^{-10}/\Omega$-cm, and the density of the photo-electrons is estimated to be of the order of $10^{8}/\mathrm{cm}^{3}$. The square root dependence of the current at high fields was not definite but depended on samples, and could not indicate that the scattering is dominated by the acoustic phonon scattering. At the higher field, there appeared no complete saturation of the current up to the maximum field measured, but a slight increase was found as in the case of CdS[5].

No instabilities by domain formations[6] or by electrode effects [7] were found. But at the high fields of $E \sim 10^{5}$V/cm, there appeared an oscillation in d^2I/dE^2 vs E characteristics. By utilizing the conventional ac-voltage modulation method, the differential conductance was recorded on a X-Y recorder. Figure(2) shows a typical trace of the second derivatives as a function of the field. The oscillatory structure can be attributed to the electron-phonon interactions in the quantized Stark ladders as follows. Recent theories of the Stark ladder resonance[4,8] have proposed an increase of the current at the field

$$E_n = \frac{\hbar\omega_o}{nae} \tag{1}$$

where $\hbar\omega_o$ is the zone center longitudinal optical phonon energy, e the electronic charge, a the lattice spacing along the field and

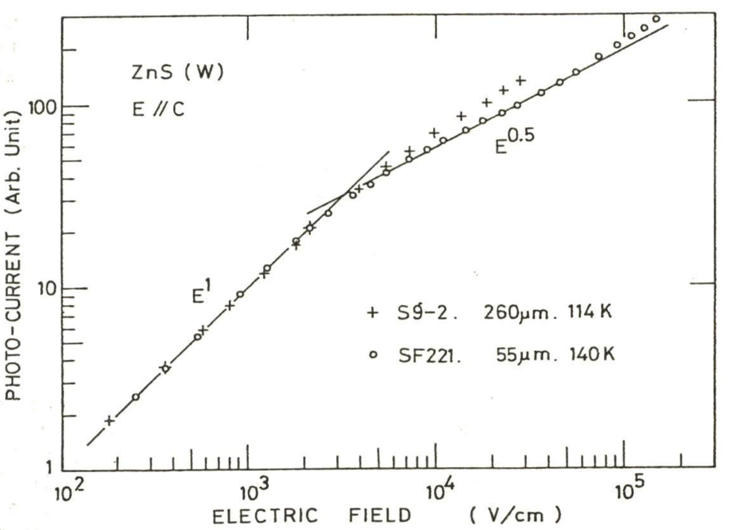

Fig. 1. Photo-current vs electric field characteristics of ZnS along c-axis

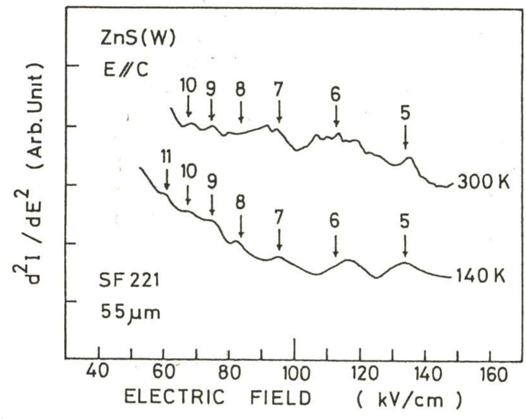

Fig. 2. Oscillation of the second derivatives of the current as a function of the field

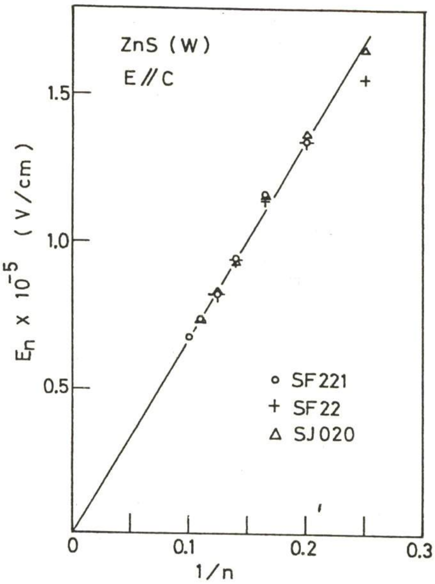

Fig. 3. Linear dependence of the critical field E_n on $1/n$

n is an arbitrary integer. The successive peaks in Fig.(2) are around at the field strength given by Eq.(1) for a hexagonal ZnS ($\hbar\omega_o \simeq 0.04$ eV, $a = 6.26$ Å [9]). To confirm this, the linear dependence of the fields at each peaks on 1/n was examined in Fig.(3), from which the optical phonon energy was determined with the aid of Eq.(1) : $\hbar\omega_o = 42.0 \pm 0.7$ meV. The arrows in Fig.(2) indicate the positions of the peaks assigned for $\hbar\omega_o = 42$ meV and $a = 6.26$ Å with the integral numbers cited. The agreement is satisfactory.

Incidentally, the Stark ladder levels are expected to be realized if the characteristic relaxation time τ_c of the electrons are large enough so as to satisfy

$$\tau_c \quad > \quad \frac{h}{aeE} \qquad (2)$$

In other words, the mobility of electrons must be large enough. Though the measurements of the mobility have not been done for the present samples, the sublinear dependence of the current on the field in Fig.(1) indicates a good quality of the crystal and a high electron mobility†. From a point of probability view, even in a material with poor electron mobility, some of the electrons can escape from the scatterings and can complete the cyclic motion in the Brillouin zone. One can study the motion of these lucky electrons if the increase of electrons by the avalanche ionization process is avoided. In fact, in the measurements of the current and the first derivative

† This point is, however, still controversial because a saturation of the photocurrent due to the elcetric field dependence of the life time has also been found in photo-conducting materials[10].

dI/dE, there have appeared no conclusive evidence of the Stark quantization, which suggests that the oscillatory component is less than 1 % of the total current.

According to the theoretical results[4,8], the amplitude of the current increase at the critical field given by Eq.(1) is not so sensitive to the number n. Therefore the appearance of peaks in Fig.(2) up to the higher order of n $\sim$ 10 ($\hbar\omega_O/n \sim 4.2$ meV) at a rather high temperature (kT $\geq$ 10 meV) is not a so surprizing result. The line shape of the second derivatives is to be dependent on the variation of the lattice temperature as well as on various scatterings other than by the optical phonons. Two curves in Fig.(2) show that the lower the temperature is the clearer becomes the line shape in good agreement with the theoretical prediction. Further studies of the line shape at a lower temperature (e.g., at liq. He temperature) are desirable to assert this point.

IV. Conclusion

The oscillation found in the second derivatives of the photocurrent of ZnS as a function of the dc electric field was due to the resonant interactions of electrons in the Stark ladders with longitudinal optical phonons. By analyzing the oscillation periodes, the optical phonon energy of the hexagonal ZnS was determined : $\hbar\omega_O$ = 42.0 ± 0.7 meV.

---

* Supported in part by the Grant-in-Aid from the Ministry of Education.

1) G.H. Wannier: Phys. Rev. 117 (1960) 432-9.
2) S. Maekawa: Phys. Rev. Lett. 25 (1970) 1175-7.
3) D. May and A. Vecht: J. Phys. C: Solid St. Phys. 8 (1975) 505-9.
4) M. Saitoh: J. Phys. C: Solid St. Phys. 5 (1972) 914-27.
5) I. Iye and K. Kajita: Solid St. Comm. 17 (1975) 957-60.
6) K.W. Böer: IBM J. Res. Dev. 13 (1969) 573-9.
7) V.S. Mylnikov and S.P. Voronin: Sov. Phys.-Semicond. 13 (1979) 215-7.
8) N. Sawaki and T. Nishinaga: J. Phys. C: Solid St. Phys. 10 (1977) 5003-15.
9) R. Marshall and S.S. Mitra: Phys. Rev. 134 (1964) A1019-25.
10) B.K. Ridley and T.B. Watkins: Proc. Phys. Soc. 78 (1961) 710-5.