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Influence of the interfacial layer on the properties of the Au/ZnSe Schottky barrier

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Résumé. — On a étudié les propriétés de la barrière Schottky Au/ZnSe par mesures J/U , C/U et photoélectriques, avec une particulière attention à l'influence de l'interface. L'évolution de la capacité, montrée en fonction de la fréquence et de la température, a été expliquée en faisant l'hypothèse de la présence d'une distribution de niveaux accepteurs de interface. Une méthode pour la détermination de leur temps de relaxation est montrée. La détermination photoélectrique de la constante diélectrique associée à la force image, s'accorde avec la présence d'une couche de ZnO à l'interface. Enfin on a observé une émission électroluminescente pour les petites valeurs du voltage direct, avec deux pics à 1,89 eV et 2,67 eV ; ils devraient être associés à l'émission de lumière respectivement par autoactivation et recombinaison entre niveaux donneurs et accepteurs.

Abstract. — The properties of the Au/ZnSe Schottky barrier have been investigated by J/U , C/U and photoelectric measurements with considerate attention given to the influence of the interface. The behaviour of the capacitance of the diodes, investigated as a function of the frequency and the temperature, has been explained by assuming the presence of one set of surface states uniformly distributed within the forbidden energy gap. By the investigation of their frequency response a method for the valuation of the relaxation time is illustrate. The photoelectric determination of the image force dielectric constant is in agreement with the presence of a ZnO layer at the interface. Finally, an electroluminescent emission has been observed at low forward voltages with two characteristic peaks at 1.89 eV and 2.67 eV. They should be related to light emission by self-activation and donor acceptor recombination respectively.

1. Introduction. — The wide band gap II-VI compounds are well known as potentially efficient visible electroluminescent materials. In the past few years much research has been done with particular interest in blue-luminescent semiconductors such as ZnS and ZnSe. In the case of ZnSe, which has the most suitable band gap value, the achievement of an efficient injection luminescence has been conditioned by the fact that is difficult to obtain a low resistivity both in p and in n-type ZnSe crystals. Nevertheless, ZnSe light emission devices has been prepared by using alternative structures for minority carrier injection such as heterojunctions [1-4], metal-semiconductor or metal-insulator-semiconductor diodes [5-10] which give light emission also in the blue spectral region. The electrical properties of the Au/ZnSe barrier have also been investigated [11-17]. It was found that even the ultra high vacuum [11] and improved etching technique [17] were unable to avoid the rise of an interfacial layer between the metal and the semiconductor. Nevertheless there exists few data concerning the

influence of such an insulating layer on the properties of the Au/ZnSe Schottky diode. The purpose of this work has been the investigation of the electrical and photoelectrical properties of the Au/ZnSe Schottky barrier particularly concerning the dependence of the barrier height from the interfacial layer and the interface states. This connection was principally studied by capacitance measurements that were carrier out as a function of the frequency and the temperature. The surface states density and the thickness of the insulating layer were estimated by using a theory developed by Cowley for MIS diodes with a thick layer and a moderate density of surface states.

2. Experimental details. — The ZnSe monocrystals that were used to prepare the Au/ZnSe diodes were furnished to us by the Electro-Optical Laboratory of the Physics Institute at the Nicholas Copernicus University of Torun (Poland). They were grown there by using the Bridgman method at high pressure and purified in molten zinc for 15 h at 1 000 °C. The In

ohmic contact was made with heat treatment at 300 °C for a few minutes in $H_2 + 6 N_2$ atmosphere. In our laboratory the Schottky barrier was prepared in the following way : (i) the surface, (111) oriented, was lapped and polished ; (ii) the ohmic surface was masked and the specimen was etched in a 10 % solution of Bromine in Methanol for 3' ; (iii) the sample was first rinsed in distilled water, methanol, and stored in isopropilic alcohol and then placed under vacuum. Before evaporating took place, the surface was slightly heated in order to clean it. Thus about 200-500 Å of gold were evaporated under a vacuum of about 10^{-6} torr in a standard oil diffusion pump equipment with nitrogen trap. The thickness of the metal was controlled by an FTM-1 crystal quartz monitor. The photocurrent measurements were made selecting the monochromatic light by an Hilgher single prism monochromator whose output intensity was separately calibrated. The capacitance measurements were achieved by a Boonton model 72-A capacitance meter working at 10^6 Hz, while a phase sensitive detection system was employed for the measurement in the range 10^2 - 10^5 Hz. Finally, the electroluminescence spectra were carried out by using the Au/ZnSe diode as light source of the monochromator and detecting the relative light intensity in output by a calibrated photo-detector.

3. Experimental results. — 3.1 CURRENT-VOLTAGE MEASUREMENTS. — A typical forward and reverse bias J/U characteristic of an Au/ZnSe diode is displayed in figure 1. As one can see, by comparison with the dashed straight line, the direct characteristic follows in a wide range the well known nearly ideal equation of the diode which is in accordance with the thermoionic emission theory thus giving :

$$J = J_0 [\exp(qU/nKT) - 1] \quad (1)$$

where n is the ideality factor of the diode and J_0 is the reverse saturation current which is equal to :

$$J_0 = A^* T^2 \exp(-q\Phi_B/nKT) \quad (2)$$

where $A^* = A(m^*/m_0)$ is the reduced Richardson constant and Φ_B is the height of the metal-semiconductor barrier. The ideality factor in the curve of figure 1 is $n = 1.5$. Values of n higher than one are generally ascribed to the presence of an interfacial layer. Therefore, the electrons have to tunnel through the barrier presented by the insulating layer causing the current for a given bias to be reduced. The effect of such an insulating layer is evidenced from a low value of the reverse saturation current density $J_0 = 3 \times 10^{-18}$ A/cm² as it results by extrapolating the linear part of the J/U characteristic reported in figure 1. One could determine the barrier height by using the experimental value of J_0 and the theoretical value of A^* . Indeed, when the ideality factor n assumes values higher than one, the J/U determination if not

Fig. 1. — Forward and reverse J/U characteristics of an Au/ZnSe Schottky diode at room temperature.

quite correct [22]. Moreover the forward current-voltage characteristics were carried out as a function of the temperature in the range 130-300 K.

Some dependence of the n value on the temperature was noticed. Besides, the Richardson plot of J_0/T^2 versus $1/T$ departed from the expected straight line, especially at low temperatures. Thus, we could not deduce the barrier height by a simple measurement of this slope. This fact can be explained by considering the presence of an additional majority-carrier-current caused by recombination of electrons at interface states [9]. In conclusion it seems reasonable to think to a mechanism for the carrier transport due to injection over the barrier according with the equation (1), though some part of the current could be due to tunneling and recombination at the interface states.

3.2 PHOTOELECTRIC MEASUREMENTS. — The photoelectric determination is the most immediate way to measure the height of a metal-semiconductor barrier. In our case, the samples were illuminated in front-wall way by light whose energy was lower than the band gap of ZnSe. Generally, when the square root of the photo-

Fig. 2. — Phototreshold plot for an Au/ZnSe Schottky diode at room temperature for different values of the reverse bias.

response per adsorbed photon is plotted as a function of the energy, a straight line should be attained whose intercept with the x -axis directly gives the energy barrier value Φ_B . In fact, according the theory of Fowler [19] the normalized photoresponse R can be expressed as :

$$(R)^{1/2} \propto (h\nu - q\Phi_B). \quad (3)$$

The Fowler plot is illustrated in figure 2 at different reverse bias. The relationship between the total Schottky barrier lowering and the applied field is illustrated in figure 3. Here the fit was fulfilled by an image force dielectric constant of 3.6 which is a value very near to the optical dielectric constant of ZnO, that is $\epsilon_\infty \simeq 4$. For ZnSe the same parameter is $\epsilon_\infty \simeq 6.1$. As it has been previously demonstrated [15], the dependence of the phototreshold value from the applied electric field allows us to estimate the lowering of the barrier at zero bias in terms of image force effect. Therefore, a lowering of the barrier height $\Delta\Phi = 0.1$ V with a phototreshold $\Phi_B = 1.65$ V were measured at zero bias.

3.3 CAPACITANCE MEASUREMENTS. — Figure 4 shows a typical C^{-2} against U curve achieved by a low a.c. signal at a frequency of 10^6 Hz. As it can be observed the intercept voltage on the x -axis results higher in respect to the value which can be carried out by photoelectric measurements previously illustrated. Generally, the linearity of the C^{-2} versus U curves allows one to assume a depletion approximation in which the charge density in the space charge region of

the semiconductor is constant and is due to ionized impurity levels alone. In this approximation, the uncompensated donor density N_D^+ can be carried out by the slope of the curves. The capacitive cut-off voltage U_0 allows one to calculate the diffusion voltage U_B and consequently the barrier height Φ_B . The presence of an interfacial layer causes an intercept voltage U_0 different than U_B but should not affect the measurement of the impurity density [9, 18, 21].

By these assumptions a donor density

$$N_D^+ = 1.2 \times 10^{17} \text{ cm}^{-3}$$

resulted which is in agreement with the value achieved by the conductivity measurements. Also an energy difference between the fermi level and the bottom of the conduction band $E_C - E_F = 0.048$ eV was obtained. At last, from the zero bias capacitance value a width of the depletion layer $W = 0.13 \times 10^{-4}$ cm was calculated.

3.4 INTERFACIAL LAYER AND INTERFACE STATES. — The capacitance of a Schottky diode is influenced by the presence of an insulating layer at the interface. In fact, if one tries to obtain the diffusion voltage by the intercept to zero of the C^{-2} versus U curves, it results a value which is generally larger than the voltage determined by the phototreshold measurements. The effect of an interfacial layer on the capacitance has been analyzed in detail by Cowley [21] giving a model for the dependence of the diffusion potential on interfacial thickness. In this theory the effect of a bias dependence of the surface states is taken into account

Fig. 3. — Total Schottky barrier lowering as a function of the applied field at room temperature. The fit by the image force theory was fulfilled with $v/v_0 = 3.6$.

Fig. 4. — Typical C^{-2} versus U characteristic of the Au/ZnSe Schottky diode performed with a measuring frequency of 10^6 Hz at room temperature.

too, describing them in terms of the Bardeen's model. According this last framework there is a continuous distribution of states at the semiconductor surface which are characterized by a neutral energy level ϕ_0 . The occupancy of the surface states is determined by the fermi level and in the 0 K approximation [21] the charge which is associated to them can be expressed by :

$$Q_{ss} = -qD_{ss}(E_F - \phi_0) = qD_{ss}(E_g - \Phi_B). \quad (4)$$

The determination of the density of the surface states was fulfilled by using a method previously reported [9]. Following this approach, D_{ss} was calculated by comparing the increase of the space charge within the depletion region required to neutralize Q_{ss} . Thus, we calculated a value of $D_{ss} = 1.3 \times 10^{11}$ states $\text{cm}^{-2} \text{eV}^{-1}$. This states density is very near to the value $D_{ss} = 2.6 \times 10^{11} \text{ cm}^{-2} \text{eV}^{-1}$ which was carried out on similar diodes and by the same approach by Lawther and Woods [9]. Ozsan and Woods [23] reported a value of $D_{ss} = 4.0 \times 10^{11}$ states $\text{cm}^{-2} \text{eV}^{-1}$, but in this last case the authors used the conductance method firstly described by Nicolian and Goetzberger [24].

The thickness of the insulating layer was estimated by us following the Cowley's analysis in the case of a thick layer and a moderate density of surface states which gives the equation :

$$U_0 = (U_B - KT/q) - \frac{U_1^{1/2}(U_B - KT/q)^{1/2}}{(1 + \alpha\lambda)} + \frac{U_1/4}{(1 + \alpha\lambda)^2} \quad (5)$$

where U_0 is the cut-off voltage in the C^{-2} versus U curve, U_B is the diffusion potential and λ is a constant describing the potential drop in the interfacial layer. The parameter U_1 and α are given by :

$$\alpha = qD_{ss}\left(\frac{\lambda_{ox}}{\epsilon_{ox}}\right) \quad (6)$$

$$U_1 = 2 q\epsilon_s N_D \left(\frac{\lambda_{ox}}{\epsilon_{ox}}\right)^2$$

where ϵ_s and ϵ_{ox} represent respectively the semiconductor and the insulating layer dielectric constant and λ_{ox} is the thickness of the interfacial layer. By using the results of the phototreshold measurements it was found that $U_B = 1.68$ V. Therefore we plotted the equation (5) as a function of λ_{ox} by assuming the values ϵ_{ox} (ZnO) = 8.1 [25] and ϵ_s (ZnSe) = 9.2 [26] for the static dielectric constants. This plot was fitted to the experimental value of $U_0 = 1.97$ V and the best fit was carried out for $\lambda_{ox} = 85 \times 10^{-8}$ cm.

Moreover the interface states can introduce a frequency dependent term in the capacitance of a MIS diode due to their rate limited charges and discharging [20].

The time response associated with the surface states is connected with the possibility to be in instantaneous

equilibrium with the metal or with the semiconductor bulk. Thus the thickness of the insulating layer by controlling the communication between the interface states and the metal could affect their time constant value τ_s . Therefore diodes with a thick insulating layer (> 30 Å), where the interface states could be at least partially in equilibrium with the semiconductor, should present a frequency dependent term in the capacitance expression [22] and the C^{-2} versus U curves should result generally not linear, at least at frequency lower in respect to the reverse of the surface states relaxation time. In the theory of Cowley it is demonstrated that also for thick layers the expression of C^{-2} versus U is linear by assuming a measurements signal frequency much larger than the reciprocal of the time constant associated with the transfer of charge between the bulk of the semiconductor and the surface states. In our diodes, how it is confirmed by the constant slope of the characteristic reported in figure 4, this last assumption proved to be valid when a frequency of 10^6 Hz was employed. At frequency lower than 10^6 Hz an increase of the cut-off voltage in the C^{-2} versus U measurements was observed. This effect could be explained by introducing a frequency dependent term in the diode capacitance equation.

We have been attempted to analyse a such effect in a more simple way by using an approach which have been employed to describe the capacitance behaviour of MIS diodes with thick insulating layer [27].

In the inset of figure 5 it is illustrated the equivalent circuit of the Au/ZnO/ZnSe diodes including the effect of the surface states and their frequency dependence on the capacitance of the diode. Here C_{ox} and C_{sc} are respectively the contribute to the diode capacitance of the insulating layer and of the space charge region of the semiconductor, C_s is the capacitance associated to the surface states and $\tau_s = R_s C_s$ represents their response time. The expression of the input admittance of a such diode is [27] :

$$Y_{in} = G_{in} + j\omega C_{in}. \quad (7)$$

By considering only the capacitive term of the equation (7) it can be verified that C_{in} for $\omega \rightarrow 0$ and $\omega\tau \gg 1$ assumes respectively the limit values C_0 and C_∞ given by :

$$C_0 = \frac{C_{ox}(C_{sc} + C_s)}{C_{ox} + (C_{sc} + C_s)} \quad (8)$$

$$C_\infty = \frac{C_{ox} C_{sc}}{C_{ox} + C_{sc}}. \quad (9)$$

The values C_0 and C_∞ are represented in figure 5 by the two dashed lines corresponding respectively to 4 055 pF and 3 090 pF. In the same figure the solid line illustrates the behaviour of C_{in} (zero bias capacitance) as a function of the frequency, equation [9]; C_{ox} , C_s and C_{sc} have been calculated by using the values of λ_{ox} , D_{ss} and W previously obtained. By fitting this

theoretical curve with the experimental points a value of the relaxation time $\tau_s \approx 10^{-5}$ s was carried out.

Finally in the figure 6 are reported C^{-2} versus U characteristics as a function of the temperature between 200 K and 340 K. Here it can be observed that the cut-off voltage shifts toward the diffusion voltage value, as determined by phototreshold measurements, when the temperature increases up to 340 K. That can be explained taking into account that as the temperature increases, the fermi level shifts towards its intrinsic value. Thus the energy difference $E_C - E_F$ increases and causes a decrease in U_B and consequently a decrease of the apparent diffusion voltage U_0 as it can be observed in the figure 6.

3.5 ELECTROLUMINESCENCE. — In figure 7 a spectrum of electroluminescence performed on a forward bias Au/ZnSe diode at 180 K is illustrated. The broad emission band is reported in literature [10] as connected to a complex zinc vacancy and aluminium ion and is known as self activated electroluminescence. The

Fig. 5. — Behaviour of the zero-bias capacitance of the Au/ZnSe MIS diode as a function of the frequency of the measuring signal. The points represent experimental values and the continuous line is the theoretical behaviour (9). The fit was achieved by $\tau_s \approx 10^{-5}$ s. In the inset are represented the equivalent electric circuits which were used for a such analysis.

Fig. 6. — C^{-2} versus U characteristics of the Au/ZnSe Schottky diode at different temperature with a measuring frequency of 10^6 Hz.

Fig. 7. — Electroluminescence spectrum of the Au/ZnSe Schottky diode at liquid nitrogen temperature. The light emission was observed at a forward voltage of $U = 1.8$ V with a current $I = 5 \times 10^{-3}$ A.

origin and the fine structure of the blue band have been discussed in detail in a recent paper [28].

4. Conclusions. — In conclusion, the presence of an insulating layer, which was characterized by electrical and photoelectrical measurements, seems fundamental in order to determinate the electroluminescence properties of the Au/ZnSe barrier. In particular notwithstanding the presence of a moderate density of surface states and a thick interfacial layer (> 30 Å), an efficient minority carrier injection mechanism has been attained at low forward bias. The tunnel current could flow through a part of the ZnO layer where the effective thickness becomes thinner because of defects or pinholes [2]. Thus the holes injected in the ZnSe by tunneling through the insulating layer give a nearly band to band recombination which at L.N.T. causes a blue band emission which is more intense and narrow in comparison to the yellow-orange self activated luminescence band. Concerning this last observation and referring to the conclusion presented in a recent paper [29] about the emission properties of ZnS diodes, it can be observed that only Schottky diodes with a thin insulating layer at the interface can rise up an intense forward bias luminescence. From this point of view, it should be interesting to continue investigations of the properties of ZnSe diodes with respect both to the nature and to the thickness of the resistive layer which can be grown accurately controlling its thickness and using free contamination ZnSe surfaces.

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