PHYSICAL REVIEW VOLUME 140, NUMBER 6A 13 DECEMBER 1965

Effect of Charged Surfaces on the Optical Absorption Edge*

DAVID REDFIELD

School of Engineering and Applied Science, Columbia University, New York, New York

(Received 28 July 1965)

Electric fields existing within the space-charge region near a charged surface of a solid are shown to be capable of significantly altering the fundamental optical absorption edge. Their effect is to produce below the gap energy an exponential tail whose slope and magnitude depend on the field strengths. Furthermore, at any given frequency in this tail, an *apparent* absorption coefficient should be observed having an inverse dependence on the sample thickness. Using representative values for the relevant quantities, it is found that this effect can produce an apparent absorption coefficient of 200 cm^{-1} at the photon energy equal to the energy gap with the tail extending below this for $\sim$0.02 eV. Some data are cited to support the suggestion that such absorption effects occur very commonly although they have not been recognized.

INTRODUCTION

IT is well known that surfaces of solids commonly acquire a charge and this charge is compensated by an equal and opposite charge distributed through a space-charge region adjacent to the surface.[1] The electrostatic field within the space-charge region frequently reaches peak values in excess of 10^5 V/cm near the surface. Thus, beneath any charged surface there exists a thin layer containing fields of sufficient magnitude to cause a measurable broadening of the fundamental optical absorption edge.[2] Such broadening, when caused by a uniform applied field, is the Franz-Keldysh effect.[3–6] The purpose of this paper is to present a calculation of the corresponding optical absorption to be expected from a surface-charge-induced analog of the Franz-Keldysh effect. A closely related effect on the reflectivity has been observed recently in several materials.[7]

The present discussion is confined to absorption at photon energies $\hbar\omega$ equal to or less than the energy gap $\hbar\omega_g$ of the ideal solid in order to avoid the spectral region in which strong bulk absorption occurs. It should be noted, however, that the process being considered is truly fundamental absorption, since it excites electrons from lower to higher bands of the solid. It differs from ordinary fundamental absorption only because the crystal wave functions are altered by the electric field.

METHOD

Evaluation of this surface-induced absorption is accomplished by the method previously developed to evaluate the effect of impurity fields.[8] The assumption is made that the electric field in the space-charge region varies only in a direction normal to the surface and at a rate slow enough so that it may be regarded as essentially constant within any thin, but macroscopic, layer parallel to the surface. This latter assumption permits the direct application of the Franz-Keldysh type of analysis to obtain a *local* absorption coefficient A as a function of field F and photon energy $\hbar\omega$. Then the total absorption coefficient α at any value of ω is found by integrating $A(\omega,F)$ over all field strengths, provided a weighting function $W(F)$ is available to describe the probability distribution function of the field. Thus

$$\alpha(\omega)=\int_0^{F_{\max}} A(\omega,F)W(F)dF. \tag{1}$$

It is clear that this is equivalent to integrating over the position coordinate x since F is a (one-dimensional) function of position. The weighting function is therefore a measure of the thickness of the layer containing a given value of F. In this simple case it is easily seen that $W(F)=(dF/dx)^{-1}$ and $F_{\max}$ is the magnitude of the field at the surface ($x=0$).

As in Ref. 8, the local absorption coefficient is computed using the relationship for direct transitions

$$A(\omega,F)=(\Omega)^{1/2}\int_{(\omega_g-\omega)/\Omega}^{\infty} |\text{Ai}(z)|^2 dz, \tag{2}$$

where $\text{Ai}(z)$ is the Airy function[9] and Ω is a measure of the field strength given by

$$\Omega=(e^2F^2/2\hbar m^*)^{1/3}$$

in terms of the electronic charge e, and the reduced effective mass of the valence and conduction bands m^*. [It should be noted that this notation differs somewhat from that of Ref. 8 and uses the expression for Ω agreeing with that of Refs. 5 and 6 rather than that of Ref. 3. Also, the value of the integral in Eq. (2) at the energy gap ($\omega=\omega_g$) should be 0.067 rather than Franz's value used in Ref. 8.]

---

* Supported in part by the U. S. Office of Naval Research.

[1] For a review of surface properties of semiconductors see T. B. Watkins, Progr. Semicond. **5**, 1 (1960).

[2] Richard Williams, Phys. Rev. **126**, 442 (1962).

[3] W. Franz, Z. Naturforsch **13a**, 484 (1958).

[4] L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 1138 (1958) [English transl.: Soviet Phys.—JETP **7**, 788 (1958)].

[5] K. Tharmalingam, Phys. Rev. **130**, 2204 (1963).

[6] Joseph Callaway, Phys. Rev. **134**, A998 (1964).

[7] B. O. Seraphin and N. Bottka, Phys. Rev. Letters **15**, 104 (1965).

[8] David Redfield, Phys. Rev. **130**, 916 (1963).

[9] National Bureau of Standards, *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegren (U. S. Government Printing Office, Washington 25, D. C., 1964), p. 446 ff.

The dimensionless frequency $(\omega_g-\omega)/\Omega$ used in Eq. 2 will be used hereafter because of its convenience and applicability to various materials, field strengths, and other related problems.

To obtain a probability distribution function for the electric fields needed in Eq. (1) it is necessary to find a solution for Poisson's equation in the space-charge region. Because such solutions depend on a number of factors (such as concentrations of fixed and mobile charges, temperature, surface charge density), several representative types were assumed and used in these calculations. It appears that the resulting optical absorption is not very sensitive to the shape of the potential distribution in the space-charge region provided that the screening length λ and bulk-to-surface potential difference φ_s are fixed.

One specific, simple example is the parabolic potential distribution which occurs in the presence of a uniform concentration of space charge. A more realistic, simple approximation to actual cases is an exponential potential $\varphi=\varphi_s\exp[-x/\lambda]$ for which $W(F)=\lambda/|F|$ and $F_{\max}=|F_s|=\varphi_s/\lambda$. Both of these forms have been used in the present calculations and show little difference in result. The numerical values given below utilized the exponential potential with which Eq. (1) takes the form

$$\alpha(f)=\tfrac{3}{2}\lambda(\Omega_s f)^{1/2}\int_f^\infty y^{-3/2}dy\int_y^\infty |\mathrm{Ai}(z)|^2 dz, \qquad (3)$$

where $f=(\omega_g-\omega)/\Omega_s$ is the dimensionless frequency referred to Ω_s, the value of Ω at the surface where $F=F_s$. This equation was evaluated numerically[10] over a range of frequencies from the energy gap ($f=0$) down until $\alpha(f)$ dropped to $\sim 10^{-5}\,\alpha(0)$.

RESULTS

This procedure gives the relative absorption as a function of frequency with parameters m^* and ω_g describing the material; φ_s is the bulk-to-surface potential difference, and λ is the range of the screening charge. The results are shown in Fig. 1 using a logarithmic scale for α; the uniform field (Franz-Keldysh) effect is also shown for comparison. It is of considerable interest that the line through the points computed for surface fields is actually straight over five decades below the absorption value at the energy gap. We thus find an exponential absorption tail of the type observed in many materials and associated with impurity fields in some cases of bulk absorption.[8] In the present case, as in other field-induced absorptions, the exponential character of the tail has its origin in the exponential-like attenuation of the wave functions within the energy gap. (The choice of an exponential potential function in the space-charge region is coincidental. A parabolic potential also leads to an exponential absorption tail, as do others.)

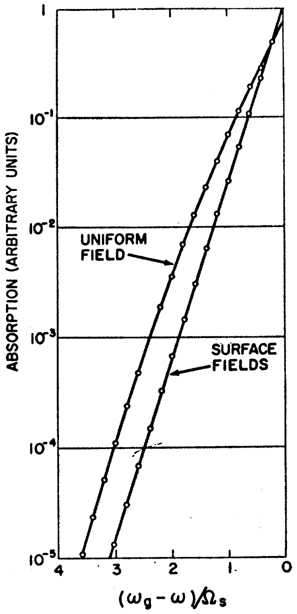

FIG. 1. Calculated optical absorption edge for frequencies at and below the energy gap.

From this general result for relative absorption it turns out to be very simple to convert to absolute magnitudes of α for any given problem. This follows from the fact that *above* the energy gap α is not affected significantly by moderate fields, so the theoretical absorption can be equated to field-free observed values. Thus for a direct-transition energy gap, the typical observed absorption above the edge can be represented by $K(\hbar\omega-\hbar\omega_g)^{1/2}$, where K determined experimentally contains all the relevant quantities such as densities of states, transition probability, etc. This can be equated to the Franz-Keldysh result in the asymptotic limit[11] of large negative f which is just $\pi^{-1}(\hbar\omega-\hbar\omega_g)^{1/2}$. In this way the Franz-Keldysh effect can be obtained merely by multiplying the relative values by πK.

To compare such calculated values with experiment, however, it is essential to recognize that the present case of surface-layer absorption differs from customary bulk absorption in one important respect. This may be readily seen from the defining relation for the absorption coefficient as the fractional rate of attenuation of light intensity I,

$$\alpha=I^{-1}(dI/dx).$$

Thus for a sample of thickness T, incident and transmitted intensities I_0 and I_T, respectively, we have (ignoring reflections)

$$\int_0^T \alpha(x)dx=\ln\frac{I_0}{I_T}. \qquad (4)$$

---

[10] The integrals were evaluated with the aid of a program developed by H. J. Bowlden. The program as used on an IBM 7094 and values of the integrals computed at 20 values of f from 0 to 4 are available.

[11] The writer is indebted to B. O. Seraphin and N. Bottka for pointing out the need for the factor of π^{-1} which was missed in previous work.

For the ordinary case of uniform, bulk absorption, α is not a function of x and this can be directly integrated, giving the standard relation $\alpha T=\ln(I_0/I_T)$.

In the present case α is a strong function of x and this standard relation is not applicable. It is useful, however, to examine the consequences of surface absorption when it is not recognized as such and is interpreted as bulk absorption. There is reason to believe that such misinterpretation may be quite common. Clearly, the use of the bulk absorption relation will lead to an *apparent* absorption coefficient

$$\alpha_{\mathrm{app}}=T^{-1}\ln(I_0/I_T). \tag{5}$$

But since (in an otherwise ideal sample) absorption below the energy gap occurs only in the two surface regions, I_T will not vary with thickness. Therefore the α_{app} will have a reciprocal thickness dependence at fixed frequency.

To obtain a theoretical value which can be compared to this α_{app}, all that is needed is to calculate the value for $\ln(I_0/I_T)$ by use of Eq. (4), whose integral is evaluated as in Eq. (1). This integral should then give the product $(\alpha_{\mathrm{app}}T)$. By this means we may assess the magnitude of the apparent absorption coefficient due to surface charge-induced effects in terms of the properties of the ideal crystal, surface conditions, and the sample thickness. An illustrative calculation of this type has been performed by choosing reasonable values of the relevant parameters and the convenient frequency $f=0$. This is, of course, the highest frequency for which an ideal material should have $\alpha=0$ and happens to simplify greatly the evaluation of Eq. (3) which becomes $\alpha(0)=0.20\lambda(\Omega_s)^{1/2}$. In terms of photon energy measured in electron volts we have $\hbar\Omega_s=7.3\times10^{-6}(m/m^*)^{1/3}F_s^{2/3}$, so that $\alpha(0)\simeq5.4\times10^{-4}(m/m^*)^{1/6}(\varphi_s\lambda^2)^{1/3}$, with φ_s in volts and λ in cm.

As an illustrative example, consider a 5-μ thick specimen of GaAs with $\varphi_s=0.3$ V and $\lambda=10^{-5}$ cm. Using the values $m^*/m=0.044$ (with the light holes dominant)[12] and[13] $K=5.8\times10^4$ cm^{-1} eV$^{-1/2}$ we evaluate Eq. (5) by means of Eqs. (4) and (3), finding at the energy gap

$$\alpha_{\mathrm{app}}(0)=2T^{-1}\pi K(5.4\times10^{-4})(23)^{1/6}\times(0.3\times10^{-10})^{1/3}\simeq200\ \mathrm{cm}^{-1},$$

where the factor of 2 is for the two surfaces which the light must traverse. This value establishes the magnitude of the vertical scale in Fig. 1 as applied to this example. The magnitude of the horizontal scale is determined by the value of Ω_s which is equivalent here to $\hbar\Omega_s=0.02$ eV. Thus the α_{app} drops by about a factor of 100 in the range 0.02 eV below the gap.

DISCUSSION

The close similarity of these results to numerous observed absorption edges suggests that surface-charge-induced absorption may be a very common occurence although heretofore unrecognized. In comparing these results with the many observations of exponential absorption tails, however, several other factors must be considered. Absorption below the energy gap could arise from surface damage in polished material, strains, transitions to impurity states, and field-induced fundamental absorption caused by bulk impurity fields. Only in this last case, very similar to the present surface field case, have exponential tails of this sort been accounted for.[8] A rough comparison can be made of the relative strength of such impurity field absorption and surface field absorption within the framework of the present work and Ref. 8. The result of this comparison is that the two types lead to equal (apparent) absorption coefficient at $\omega=\omega_g$ when

$$T^{-3}\varphi_s\lambda^2=2.5\times10^{-10}N^{2/3},$$

where T and λ are in cm, φ_s in volts, and N is the impurity concentration in cm^{-3}. Unfortunately, this relation is difficult to verify, chiefly because λ is seldom known well and can be a complicated function of N.

Surface damage due to polishing has often been hypothesized as the cause of thickness-dependent, exponential absorption tails, but there is no evidence to confirm this. In fact, such surface layers would lead to a T^{-1} dependence by the same arguments as used here, although there is no basis for an exponential spectral dependence. There has been one report of an observed inverse thickness dependence in ZnTe and this was ascribed to surface damage.[14] But when these same samples were etched sufficiently to show fine structure near the absorption edge, a strong thickness dependence was still evident.[14]

In the most detailed study of the absorption edge of GaAs, the thinner samples had appreciably higher values of α and internal strains were invoked to explain this observation.[15] Here, too, there is no evidence to support such a hypothesis for the freely suspended samples which are generally thought to be relatively strain-free.

The magnitudes of α near the energy gap in the last two cases cited were substantially greater than the 200 cm^{-1} found in the present illustrative estimate. If surface fields are responsible, this indicates that both groups of materials had very long screening lengths ($>10^{-4}$ cm). Their very high resistivities make this conjecture fairly reasonable.

Finally, it is clear that for very thin specimens $\lambda\simeq T$, the two space-charge regions will interact and the T^{-1} relation should fail. This was observed in the work on ZnTe.[14] It is also possible that the absorption tails caused by surface fields may be temperature-dependent if the screening length changes with temperature.

---

[12] H. Ehrenreich, J. Appl. Phys. (Suppl.) **32**, 2155 (1961).

[13] I. Kudman and T. Seidel, J. Appl. Phys. **33**, 771 (1962).

[14] E. Loh and R. Newman, J. Phys. Chem. Solids **21**, 324 (1961).

[15] M. D. Sturge, Phys. Rev. **127**, 768 (1962).