PHOTOEXCITATION AND PHOTOIONIZATION OF NEUTRAL MANGANESE ACCEPTORS IN GALLIUM ARSENIDE

R. A. Chapman and W. G. Hutchinson
Texas Instruments Incorporated, Dallas, Texas
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Transitions to loosely bound excited-hole states of the manganese acceptor and photoionization to the valence band are observed. The manganese ionization energy is consistent with that predicted from conduction-electron capture luminescence, but optical-phonon—assisted transitions are lower in intensity.

The excited-state spectra and ground-state binding energies of acceptors and donors in germanium and silicon,[1] effective-mass theories for the acceptor states,[2] and the photoionization cross section and theory[3] for many of the acceptors have been extensively investigated. In contrast, the excited states of donors and acceptors in the III-V compound semiconductors have not been previously observed with the exception of magneto-optical studies of donors in indium antimonide.[4] This lack of data may stem from the generally lower purity of the III-V semiconductors and the possible existence of an exponential tail on the band edges.[5]

Phonon-coupling effects on both (1) electron-capture luminescence[6] and (2) hole photoexcitation[7] and photoionization have been treated in terms of phonon coupling with the hole trapped in the neutral acceptor, with the coupling increasing inversely with the Bohr radius of the trapped hole.[6] Electron-capture recombination luminescence due to electron capture by neutral manganese already has been observed in gallium arsenide.[8] Therefore, the present infrared-absorption study of hole photoexcitation and photoionization of neutral manganese in gallium arsenide provides the first opportunity to compare phenomena (1) and (2) in a direct band-gap material.[9]

Electron capture by manganese gives a spectral peak at 1.4089 eV plus lower energy peaks due to the emission of LO phonons (36 meV each). The intensities of the n-phonon—assisted peaks follow a Poisson distribution $(\bar{N}^n/n!) \times \exp(-\bar{N})$, where $\bar{N}$ is the average number of optical phonons emitted. The photoluminescence spectrum of manganese in gallium arsenide[8] requires $\bar{N}=0.43$. If the large phonon coupling required for this value of $\bar{N}$ is due to the hole trapped in the neutral manganese center, one would expect an only slightly smaller phonon-coupling effect on infrared processes in which a hole is taken from this same neutral ground state to a loosely bound, large-radius excited state.[6,7] This expectation is not borne out by the present experiment.

The manganese-doped gallium arsenide used in the present study was pulled using a Czochralski technique which has generally provided residual impurity concentrations near mid-10^{15}/cc. The 77°K Hall mobility and carrier concentration were 910 cm^2 V sec and 6.3×10^{12}/cc. Measurements at 125°C indicated that the carrier concentration saturates near 4×10^{17} (the neutral manganese concentration). The photoabsorption coefficient was derived by comparing the transmission through 580- and 370-μ-thick samples of GaAs held near 10°K. A copper-doped germanium detector was utilized. This technique has been previously described.[10]

Figure 1 shows the photoabsorption coefficient and cross section for the 4×10^{17}-Mn/cc GaAs sample. The excited-state spectra of acceptors in gallium arsenide and germanium should

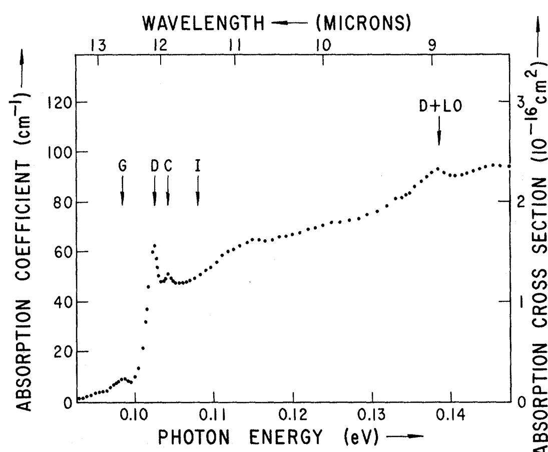

FIG. 1. Photoabsorption coefficient and cross section for manganese-doped gallium arsenide in the region near threshold. The photoexcitation resonances are labeled G, D, and C as with acceptors in germanium. D + LO is due to LO-phonon emission during the D photoexcitation.

be similar because both semiconductors have large spin-orbit splitting of the valence bands.[2] The excited-state photoexcitation resonances at 0.098_5, 0.102_5, and 1.04_2 eV are denoted by G, D, and C in Fig. 1 as has been customary with germanium acceptors. The widths of G and D are roughly 20 meV. Presumably, the use of lower manganese concentration and higher mobility GaAs would permit the detection of the B and A resonances seen in germanium acceptors.[10] The residual absorption seen overlapping the resonances may be due to an exponential tail on the valence band.[5] The small peak at 0.138 eV labeled "D+ LO" is due to photoexcitation to the same state as in the D transition but with the emission of an LO phonon. Experiments at 6°K showed an additional C+ LO peak and a suggestion of a G + LO peak. The additional small hump in the data curve near 0.115 eV may involve transverse acoustic phonons as seen in photoluminescence. The separation of the excited states (G-D = 4.0 meV and C-D = 1.7 meV) is a factor 2.3 times larger than for acceptors in germanium[1,10]; thus the binding energies of these states in gallium arsenide can be approximated[11] by multiplying the theoretical values for germanium[2] by 2.3. Using this technique, the extrapolated ionization threshold ("I" in Fig. 1) was determined to be 0.108 ± 0.002 eV. The sum of this ionization threshold and the zero-phonon photoluminescence peak is 1.517 ± 0.002 eV in general agreement with the GaAs band gap of 1.521 eV.[12]

Figure 2 shows the photoionization coefficient and cross section over a wider range of photon energies. Some scatter in the data was observed in the 7-μ region presumably due to varying absorption caused by water vapor in the beam path (this portion of the curve is dashed in Fig. 2). The arrow at $I+\Delta$ shows the ionization threshold to the spin-orbit split-off (by 0.339 eV[13]) valence band in gallium arsenide.

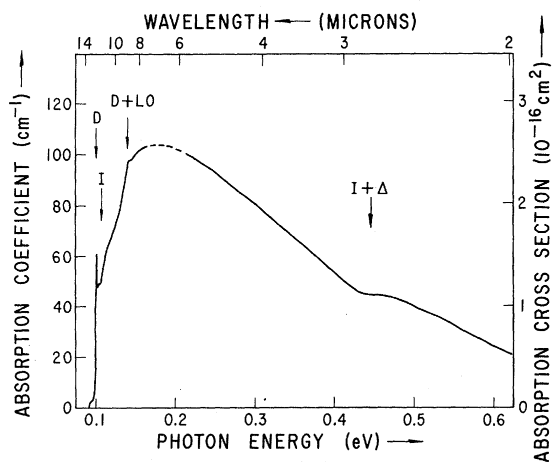

FIG. 2. Photoabsorption coefficient and cross section (detail surpressed near threshold) for manganese-doped gallium arsenide. Notation as in Fig. 1 with Δ being the spin-orbit splitting of the valence bands in gallium arsenide.

The integrated cross section for the resonances G, D, and D + LO are approximately 0.03 $\times 10^{-18}$, $0.2_5 \times 10^{-18}$, and 0.03×10^{-18} eV cm^2, respectively. The values for G and D are quite similar to those obtained for mercury-doped germanium, thus strengthening the identification of these lines. No phonon-assisted photoexcitation has been observed in silicon or germanium but has been observed in type-IIb diamonds.[7] The ratio of the oscillator strength in the one-phonon–assisted photoexcitation to that in the total no-phonon–assisted photoexcitation is in the range 0.1-0.15. Since this ratio is 0.43 in electron-capture recombination luminescence, this suggests that a more complete theory of phonon coupling for two processes may be required.

The integrated photoionization cross section is 8×10^{-17} eV cm^2 yielding an oscillator strength of 1.3, consistent with the oscillator strength of 1 expected for a single-hole acceptor.[10] The shape of the photoionization cross section is similar to that seen for indium-doped silicon[3] and mercury-doped germanium,[10] both of which have ground-state binding energies similar to that of manganese. Thus, there are also no appreciable effects of phonon assistance or photoionization of the manganese center.

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TEMPERATURE-MODULATED REFLECTANCE OF GOLD FROM 2 TO 10 eV

W. J. Scouler
Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts
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The temperature-modulated reflectance, $\Delta R/R$, of gold films has been measured from 2 to 10 eV. The range of modulated reflectance experiments is thus extended into the vacuum ultraviolet. The observed structure, which is much more complex than the conventional reflectance spectra, is of considerable significance to band-structure studies.

The results to be presented in this paper indicate that a recently reported method of modulating the reflectance of semiconductors[1] is a very sensitive way of studying the optical properties of metals. In this technique a pulsed electric current is passed through a sample while synchronously detecting the modulated reflectance $\Delta R/R$. The method has some obvious experimental advantages over the electroreflectance method[2,3] in that (1) the photon energy limit is not restricted by absorption in the electrolyte or electrode; (2) the sample may be cooled to lower temperatures; and (3) there is no possible chemical reaction with an electrolyte. Its advantages over the piezoreflectance method[4] are not as pronounced except that it may be experimentally simpler, particularly for low-temperature work. It appears to be as sensitive, on the basis of published results.[4] As the discussion to be presented will show, each technique offers different information and all methods should be used in order to be able to understand best the band structure of solids.

This paper presents results for gold, one of the noble metals which are of particular interest since there is considerable discussion about the interpretation of optical measurements and photoemission results and their relation to the band structure.[5] Experimentally, the films are easy to prepare and are stable against oxidation.

The gold films, about 2000 Å thick, were evaporated onto 0.150-mm glass substrates. Other substrates such as Mylar and silicon were used and gave substantially identical results. The samples were then cemented to a liquid-nitrogen—cooled heat sink using silicone vacuum grease mixed with silver powder to improve its thermal conductivity. Electrical leads were silver cemented to the sample. The optimum pulse rate was about 15 Hz at unit duty cycle with 6 A passing through the sample. It was observed that at higher pulse frequencies the signal deteriorated, indicating that the modulation effect is thermal. This is reasonable since the slow pulsing frequency gives the sample and substrate, with their fi-