Cardona M, Shaklee K L & Pollak F H. Electroreflectance at a semiconductor-electrolyte interface. *Phys. Rev.* **154**:696-720, 1967.
[Department of Physics, Brown University, Providence, RI]

The paper describes a simple method for determining interband critical points (i.e., energy gaps) in semiconductors based on the modulation of the reflectivity produced by an AC voltage applied to a semiconductor-electrolyte interface. The energies of a large number of critical points of tetrahedral semiconductors are listed. [The *SCI*® indicates that this paper has been cited in over 430 publications since 1967.]

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"After working for five years at RCA on interband critical points and optical reflectivity of semiconductors, I moved to Brown University in 1964. That field was getting dry: the cream had already been skimmed. With a university instructor, Fred Pollak, and a graduate student, Kerry Shaklee, I began, in 1965, to look for new ideas. Fred was an expert in semiconductors under uniaxial stress. We tried to modulate the reflectivity with a periodically modulated stress but were swamped by a large featureless background. Our system was much too crude.

"In the meantime, the first paper on electroreflectance appeared.[1] We tried to build a Seraphin-type cell but were not successful. A paper by Dick Williams,[2] in which he was able to modulate the transmission of CdS by means of a field applied to a sample immersed in an electrolyte, crossed our minds. We put Kerry to work and went home on a Saturday afternoon. Within hours, Kerry called and told me he had observed the now classical electroreflectance signal of the E_1-$E_1+\Delta_1$ gaps of Ge. The original results were first published in reference 3. The *Citation Classic* discusses the detailed measurements for Ge and for many other semiconductors.

"The secrets of the success were the idea of using an electrolyte, Kerry's experimental ability, and the PAR lock-in amplifier. The rest of the equipment was a cheap monochromator, a quartz-iodine lamp, a photomultiplier, and a glass beaker with water and salt. The beaker was soon to acquire a silica window for ultraviolet operation. A cannibalized Heathkit recorder was quickly added to the system as an analog computer to perform the $\Delta I/I_o$ division. In those days, when digital equipment was not as omnipresent as now, this was a very effective device. When its monotonous chatter stopped, we heard that something was wrong and rushed to the equipment.

"The reasons for the high number of citations are, on the one hand, the simplicity of the technique, which was within reach of any college teaching lab. On the other hand, the large number of critical points listed for many tetrahedral semiconductors together with their band structure assignments makes the paper very useful. These numbers were needed to check the large amount of theoretical calculations which were becoming available. Because of its simplicity, the empirical pseudopotential method pioneered by J.C. Phillips and M.L. Cohen[4] was an ideal counterpart of the electroreflectance technique.

"A number of other reflectance modulation methods appeared quickly after our work. The modern techniques of rotating analyzer ellipsometry (D.E. Aspnes[5]) and resonant Raman scattering[6] can be considered as 'latter day' modulation methods.

"In view of these newer developments, electrolyte electroreflectance has lost importance as a tool for basic research. However, it is used routinely for materials characterization and for studies of semiconductor-electrolyte interfaces.[7] The work on modulation spectroscopy done before 1969 is reviewed in reference 8.

"Partly because of this work, I have been awarded the 1984 Frank Isacson Prize of the American Physical Society and the 1982 Narcís Monturiol Medal of the Generalitat de Cataluña."

1. **Seraphin B O & Hess R B.** Franz-Keldysh effect above the fundamental edge in germanium. *Phys. Rev. Lett.* **14**:138-40, 1965. (Cited 130 times.)
2. **Williams R.** Electric field induced light absorption in CdS. *Phys. Rev.* **117**:1487-90, 1960. (Cited 60 times.)
3. **Pollak F H, Cardona M & Shaklee K L.** Piezoelectroreflectance in GaAs. *Phys. Rev. Lett.* **16**:942-4, 1966. (Cited 35 times.)
4. **Cohen M L & Bergstresser T K.** Band structures and pseudopotential form factors for fourteen semiconductors of the diamond and zinc-blende structures. *Phys. Rev.* **141**:789-96, 1966.
5. **Aspnes D E & Studna A A.** Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV. *Phys. Rev. B* **27**:985-1009, 1983.
6. **Cardona M.** Resonance phenomena. (Cardona M & Güntherodt G, eds.) *Light scattering in solids. II.* Berlin: Springer-Verlag, 1982. p. 19-178.
7. **Pollak F H.** Spectroscopic and surface analytical measurements to probe the semiconductor/electrolyte interface. (Wallace W L, Nozik A J & Deb S K, eds.) *Photoelectrochemistry, fundamental processes and measurement techniques.* Pennington, NJ: Electrochemical Society, 1982. p. 608-21.
8. **Cardona M.** *Modulation spectroscopy.* New York: Academic Press, 1969. 358 p.

