This Week's Citation Classic

Trumbore F A. Solid solubilities of impurity elements in germanium and silicon.
Bell Syst. Tech. J. **39**:205-33, 1960.
[Bell Laboratories, Murray Hill, NJ]

Solid solubility data are reported for various impurity elements in germanium and silicon. These results and other available data are summarized and critically evaluated to yield sets of solidus and solvus curves for the major dopants in these semiconductor host materials. [The *SCI*® indicates that this paper has been cited in over 350 publications since 1961.]

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November 15, 1982

"On joining the infant solid-state revolution at Bell Laboratories in 1952, I was immediately seduced by the beauty of those early germanium and silicon single crystals, the forerunners of today's bologna-size ingots from which the ubiquitous silicon chip is manufactured. The control of the distribution and doping levels of impurities was, and still is, fundamental to the fabrication of these chips and other solid-state devices; hence, the frequent citation of the impurity solubility data compiled in this *Citation Classic*. Happily, my own work involved the growth of crystals from solutions of the semiconductors in the impurity elements, thus indulging my fascination with crystals. One growth technique required up to three months to grow suitable crystals. The growth and the subsequent chemical and electrical analyses of these hard-won crystals to yield the solubility data involved the cooperation of many highly competent colleagues in a truly golden era at Bell Laboratories.

"Fortunately, my efforts were directed primarily toward the more soluble impurities (e.g., gallium and arsenic). When Esaki,[1] in Japan, invented the tunnel diode, a device requiring heavily doped semiconductors, I became an instant authority on tunnel diode materials by simply supplying my device-oriented colleagues with crystals from my desk drawer. Replenishing the supply proved troublesome, however, with repeated unsuccessful attempts to pull single crystals of very heavily arsenic-doped germanium. One evening, in despair, I suggested to my colleague Ed Porbansky that he not turn off the crystal pulling machine. The next morning we found a gorgeous, uniquely shaped single crystal which had grown due to evaporation of arsenic, the solvent! Processing these crystals resulted in a tunnel diode patent with Ralph Logan and William Spitzer[2] which nearly brought the wrath of the physics community down upon us. A paper describing the work was in press in a well-known physics journal when the patent application was belatedly classified secret by a branch of the armed forces. (Why, we never knew.) Reason prevailed, fortunately, and the patent was declassified just in time to prevent a proposed impounding of the entire pressrun of the journal in question!

"Later, I extended my work on impurities to gallium phosphide. Unexpectedly, this side project yielded crystals with very interesting luminescence properties and I found myself in another collaborative effort with Logan, Harry White, and Michael Kowalchik which led to the world's most efficient light emitting diodes (LEDs).[3] Contrary to a widely disseminated newspaper account of our work, the LEDs were not suitable for traffic lights and we had to refuse a request to license our LEDs for lighthouse beacons! In 1970, in recognition of the work on impurities in the various semiconductors, I received the first Electronics Division Award of the Electrochemical Society. The *Citation Classic* was also reprinted in a book in 1964.[4]

"This commentary would be incomplete without acknowledging Carl Thurmond, who inspired this paper. His tireless and stimulating efforts in educating, consulting, and arguing with his colleagues on materials problems represented a truly significant contribution to the solid-state revolution which has not been adequately recognized outside of Bell Laboratories."

1. **Esaki L.** New phenomenon in narrow germanium *p-n* junctions. *Phys. Rev.* **109**:603-4, 1958.
2. **Logan R A, Spitzer W G & Trumbore F A.** *Method for increasing the doping level of semiconductor materials.* US patent 3,111,433. 19 November 1963.
3. **Logan R A, White H G & Trumbore F A.** *P-N* junctions in GaP with external electroluminescence efficiency ~2% at 25°C. *Appl. Phys. Lett.* **10**:206-8, 1967.
4. **Trumbore F A.** Solid solubilities of impurity elements in germanium and silicon. (Levine S N, ed.) *Micro- and thin-film electronics: readings.* New York: Holt, Rinehart and Winston, 1964.