

Manuel Cardona's Contributions to Semiconductor Technology: A View from Industrial and Applied Physics

Stefan Zollner

A speaker at a conference last year said that Manuel Cardona “knew more about the basic nature of semiconductors than anyone in the world”. As a student in Stuttgart, it certainly felt that way. The combination of Manuel’s knowledge and wisdom, the experience of his students and visitors and other scientists in the institute, and the well equipped library made Heisenbergstrasse a wonderful place for Ph.D. thesis research. I also made personal connections there, which have influenced my career in industry and academia for more than 20 years.

While Manuel’s contributions to basic solid-state physics have been well documented and will certainly be addressed elsewhere in this book, it is also worthwhile to stress Manuel’s contributions to semiconductor technology. Our world is very different today compared to the 70s, when Manuel began his long tenure in Stuttgart. Computers are now commonplace and we increasingly rely on smartphones and tablets for everyday activities like booking travel, online purchases, gathering information, getting directions, etc. Manuel and his students and visitors made very significant contributions to the semiconductor process technologies, which have enabled these high-tech products. It took, of course, thousands of micro-innovations to create these technology platforms. A few of these, however, including some very important ones, clearly carry Manuel’s fingerprints.

The industrial contributions of an academic scientist start with training students who choose industrial careers. Manuel’s own career began in industry, at RCA in Princeton and Zurich, and included many visits to the industrial labs at IBM and Xerox. Today, these industrial physics labs are mostly in the past, unfortunately, but the legacy of Manuel’s students in industry continues. Manuel actively encouraged his students and postdocs who sought an industrial career. A few names worth mentioning are Peter Lautenschlager (aerospace), Diego Olego (Phillips Healthcare), Tobis Ruf (Bosch), Uwe Schmid (software), Jens Kircher (Bosch), Thorsten Heyen (Wacker, Infineon), Ran Liu (Motorola), Andreas Goebel (Acorn Technologies), Wolfgang Kauschke (Lucent Alcatel), Gerhard Fasol (Hitachi), Stefan Zollner (Motorola, Freescale, IBM). I am proud to say that I am continuing the tradition of training students for industrial careers: My first Ph.D. student Lina S. Abdallah, after writing a thesis on spectroscopic ellipsometry of Ni-Pt alloys, just took a position with Intel in Oregon as a lithography engineer.

Manuel Cardona liked to stay in touch with his students in industry. He visited Ran Liu and me at the Motorola Process and Materials Characterization Lab in Mesa, AZ, around 2000, while we prepared for the International Conference on the Physics of Semiconductors (ICPS, his favorite conference series), held in Flagstaff in July 2004. He encouraged us to include industrial topics and issues in the planning of the 2004 ICPS, following a long tradition from the 70s and 80s, which, unfortunately, has gone out of fashion at the ICPS. While other scientists frowned upon the March meeting activities of the Forum on Industrial and Applied Physics (FIAP, a unit of the American Physical Society), which I represented as Chair and later as APS Councillor and Executive Board Member, Manuel was a frequent active and passive participant in our sessions. He had a keen interest in the applications of the basic semiconductor science he understood so well. At the 2002 APS March meeting in Indianapolis, when we expected vacuum-ultraviolet (157 nm) lithography to push the limits of CMOS scaling, Manuel gave the opening invited talk “Vacuum ultraviolet spectroscopy: Classical examples and recent results” in a FIAP invited session on “VUV Optical Science and Measurements”. He clearly understood the issues we were struggling with, especially the stress-induced birefringence and spatial dispersion of calcium fluoride just below the band gap. He offered important insights and pointed out issues (which eventually killed the VUV lithography technology).

Manuel Cardona received his Ph.D. in applied physics at Harvard in 1959, following a thesis with Bill Paul on the pressure and temperature dependence of the dielectric constant of semiconductors. (Since German universities abandoned academic regalia in the late 60s, Manuel’s Ph.D. students in Stuttgart were allowed to wear Manuel’s Harvard gown during the parties following their thesis defense. These parties were an important element of the culture at the MPI and allowed for integrating a very diverse group of scientists.) It is not surprising that pressure, strain, alloy composition, and temperature became important themes for Manuel’s research throughout his career. Manuel knew how to manipulate materials through external stimuli to unlock their secrets.

Strain is also an important component of modern complementary-metal-oxide semiconductor (CMOS) technologies. To achieve scaling of CMOS devices following Moore’s Law, it is necessary to reduce the channel resistance with each generation. By applying a process-induced stress to the channel, it is possible to split bands and modify the effective masses of electrons and holes. For electron-based NMOS devices a strain along the (100) direction splits the three equivalent directions into a doublet and a singlet. For the proper sign of the stress, the singlet becomes the ground state, which reduces intervalley scattering, the dominant scattering mechanism under high electric fields. Similarly, stress will split the heavy and light hole bands. Choosing a suitable stress, it is possible to populate the holes in the light hole band, which has a lower effective mass and a higher mobility than the heavy hole band in Si.

The most powerful method to achieve stress is to dry-etch a divot in the silicon source-drain areas of devices, followed by selective epitaxy of a silicon-germanium (for the PMOS) or silicon-carbon alloy (NMOS) using chemical vapor deposition.

The difference in the lattice constant between the Si:Ge (or Si:C) alloy and pure Si causes a uniaxial stress in the channel, which reduces the channel resistance. These effects can easily be understood using $\mathbf{k}\cdot\mathbf{p}$ theory (another one of Manuel's favorite topics) and are incorporated into commercial device simulators. (Another method to reduce device resistance is with ultrahigh doping by ion implantation followed by laser annealing, one of the thesis topics of Luis Viña.)

Right across the hall from his office on the seventh floor, Manuel had a cabinet containing his famous sample collection. Among the most valuable pieces were bulk silicon-germanium crystals grown in the 1950s at RCA. Even today, these would be very unique pieces. Nobody grows such alloys anymore as bulk crystals. Silicon-germanium alloys were crucial to our understanding of the band structure of silicon and germanium. Manuel and his students and guests (especially Isabel Alonso, Josef Humlicek, and J.B. and M.A. Renucci) established a database of basic properties of silicon-germanium alloys, which formed the basis for the introduction of silicon-germanium alloys into mainstream cellphone production at Motorola in the late 1990s. Manuel was also a heavy user of the crystal growth laboratory at the institute, especially after the discovery of high-temperature superconductivity.

Manuel also collaborated with scientists who had epitaxial crystal growth capabilities, especially Gerhard Abstreiter (and later Karl Eberl) on silicon-germanium and with Klaus Ploog on compound semiconductor heterostructures. Pseudomorphic growth of epitaxial layers produces biaxial stress, which causes shifts and splitting of phonon and electron energies, a common theme for Manuel's students.

During the late 1980s, Manuel's *Abteilung* could roughly be split into five groups by their experimental methods (Raman, ellipsometry, photoemission) and their class of materials (semiconductors and oxide superconductors). As a student, I stayed away from oxides as much as possible, but they have now become the focus of my research at New Mexico State University. I was not introduced to the spectroscopy of oxides until I joined Ran Liu at Motorola in Mesa, AZ, in 1997. During this time period, semiconductor companies started to contemplate replacing silicon dioxide as the gate oxide material in CMOS devices with complex metal oxides. These oxides have a higher dielectric constant than SiO_2 and thus reduce the leakage current (by quantum mechanical tunneling) through the gate oxide. Ran Liu and I had the benefit of being aware of 40 years of research by Manuel on the dielectric constant and its relationship with the vibrational and electronic degrees of freedom of materials. We published many papers on Raman spectroscopy and ellipsometry of metal oxides, especially SrTiO_3 and HfO_2 . One of the blueprints for our work was a paper by Ran Liu (written as part of his thesis in Stuttgart) on the phonon symmetries and frequencies of $\text{YBa}_2\text{Cu}_3\text{O}_7$, one of the most highly cited physics papers in 1988.

Raman spectroscopy was certainly the workhorse in Manuel's laboratories in Stuttgart. Thanks to the efforts of his group, Raman spectra are well understood for many classes of materials. With the arrival of commercial easy-to-use Raman spectrometers (especially by Renishaw), Raman spectroscopy became an important

metrology technique for the semiconductor industry. Manuel's most highly cited journal article addresses the hydrogen-related Raman spectra in amorphous silicon, an important example of the Raman metrology that was used heavily at Motorola factories for process control. Ran Liu also developed a technique, where he could determine the Si-Si Raman frequency with an accuracy of 0.01 cm^{-1} and a spatial resolution of 0.3 micrometers (employing UV optics in the spectrometer, mirrors and detectors with UV coatings, and the 325 nm line of a He-Cd laser). This allowed two-dimensional stress mapping of process induced strain in CMOS devices, an important result for device and process simulations.

In summary, Manuel Cardona's research had a comprehensive, lasting, and important influence on the development of semiconductor technology and scaling of CMOS devices following Moore's Law. Some of his students and postdocs (like Meera Chandrasekhar) may not even have been aware of the impact of their research. Industrial semiconductor engineers do not usually look for the provenance of a scientific result, but my classmate Ran Liu and I would often recognize Manuel's influence on our work at Motorola.

The references below list my choice for the top ten industrial physics papers authored by Manuel Cardona. Some of these papers are among Manuel's most highly cited papers. It is clear that his research has had a very profound impact on semiconductor technology.

References

1. M.H. Brodsky, M. Cardona, J.J. Cuomo, Infrared and Raman spectra of the silicon-hydrogen bonds in amorphous silicon prepared by glow discharge and sputtering. *Phys. Rev. B* **16**, 3556 (1977) (1527 citations in Google Scholar (#1))
2. F.H. Pollak, M. Cardona, Piezo-electroreflectance in Ge, GaAs, and Si. *Phys. Rev.* **172**, 816 (1968) (786 citations in Google Scholar (#3))
3. F. Cerdeira, C.J. Buchenauer, M. Cardona, F.H. Pollak, Stress-induced shifts of first-order Raman frequencies of diamond-and zinc-blende-type semiconductors. *Phys. Rev. B* **5**, 580 (1972) (756 citations in Google Scholar (#4))
4. M. Cardona, Optical properties and band structure of SrTiO_3 and BaTiO_3 . *Phys. Rev.* **140**, A651 (1965)
5. R. Liu, C. Thomsen, W. Kress, M. Cardona, B. Gegenheimer, F.W. De Wette, J. Prade, A.D. Kulkarni, U. Schröder, Frequencies, eigenvectors, and single-crystal selection rules of $k = 0$ phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: Theory and experiment. *Phys. Rev. B* **37**, 7971 (1988)
6. L. Vina, M. Cardona, Effect of heavy doping on the optical properties and the band structure of silicon. *Phys. Rev. B* **29**, 6739 (1984)
7. M. Cardona, W. Paul, H. Brooks, Dielectric constant of germanium and silicon as a function of volume. *J. Phys. Chem. Solids* **8**, 204 (1959)
8. J.B. Renucci, M.A. Renucci, M. Cardona, Volume dependence of the Raman frequencies of Ge-Si alloys. *Solid State Commun.* **9**, 1651 (1971)
9. P.Y. Yu, M. Cardona, Spatial dispersion in the dielectric constant of GaAs. *Solid State Commun.* **9**, 1421 (1971)
10. D.E. Aspnes, M. Cardona, Strain dependence of effective masses in tetrahedral semiconductors. *Phys. Rev. B* **17**, 726 (1978)