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Dislocations as electrically active centres in semiconductors—half a century from the discovery

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Abstract
In the paper I recount a fascinating story, beginning in the early fifties—in the last century—when the nascent semiconductor revolution became entangled with in-depth exploration of dislocations in semiconductor crystals.

1. The very beginning

In 1934 Taylor [1], Orowan [2] and Polanyi [3] introduced the concept of crystal dislocation. This concept allowed an understanding of the plasticity of metals. Fourteen years later, the transistor was invented and a new era was begun in the development of our technological society. At that time, the crystal dislocation was more a conceptual trick than a physical reality. But it was very soon recognized that semiconductors allowed for easy visualization of dislocations in crystals and, moreover, that dislocations played a very specific role in semiconductor crystals suitable for electronics use.

Therefore, it is not surprising that big industrial laboratories implementing new transistor technologies, such as Bell Telephone Laboratories and General Electric Research Laboratory, became particularly interested in dislocations in semiconductors. It is significant that William Shockley—one of inventors of the transistor at Bell Telephone Laboratories—contributed considerably to the development of the physics of dislocations. He was the first to notice in 1953 that unsaturated bonds appearing at edge dislocations in covalent crystals could form a one-dimensional energy band partially filled with electrons [4].

On the other hand, many university laboratories nominally concerned in metal physics began to engage more and more in semiconductor work. A prominent example of those was the *Institut für Metallphysik der Universität Göttingen*, headed by Peter Haasen. When Helmut Alexander took over leadership of the *Abteilung für Metallphysik der Universität zu Köln*, the latter also became an important research centre in the study of dislocations in semiconductors. But let me come back to the beginning of the story.

In 1952 a one and a half page communiqué entitled 'Plastic deformation of germanium and silicon' written by Gallagher [5] from General Electric appeared in the 88th volume of

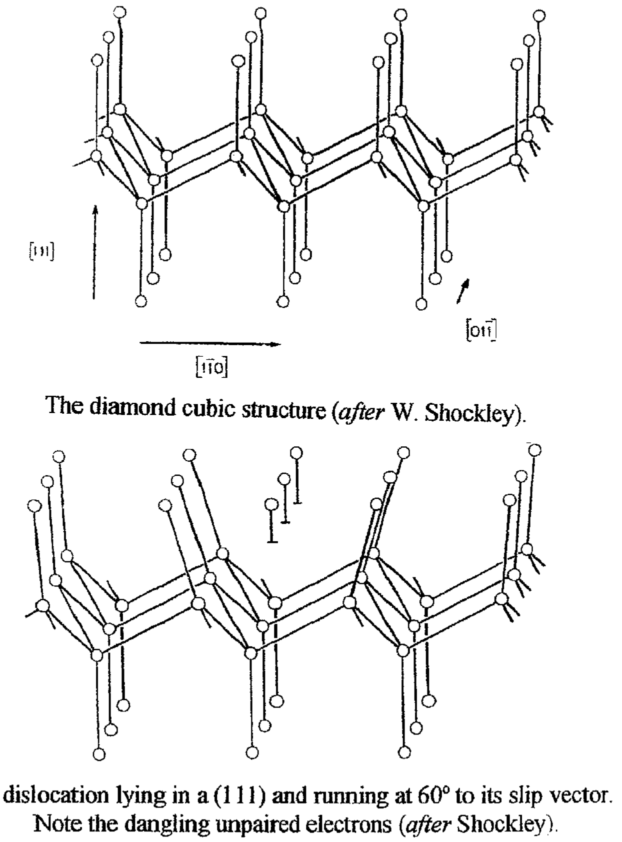

Figure 1. The original figure from Read's paper [11] demonstrating perfect diamond structure (upper) and one containing a 60° dislocation (bottom).

Physical Review. It was dated 18 June, just 50 years ago, and this is the anniversary that we are celebrating. In this communiqué, the author announced that he had succeeded in achieving plastic deformation of germanium and silicon crystals at elevated temperatures. He also reported that the resistivity of germanium increased upon deformation and that the lifetime of photo-injected carriers was drastically reduced. This article was followed by another one, written by Frederick Seitz [6], who, commenting on Gallagher's results, wrote that they provide a remarkable insight into the ductility of materials in general, as well as that of valence crystals in particular.

In the following years many scientists in the United States reported on similar observations. These were the people whose names were well known in that pioneering period of semiconductor electronics, such as Pearson, Logan and Bardsley [7–10]. Their results showed that acceptors and recombination centres were introduced to germanium crystals by deformations, which were presumably connected with dangling bonds in dislocation cores; see figure 1.

In 1954, Read [11] at Bell Telephone Laboratories developed the first theory concerning electrical properties of dislocations in semiconductors. He derived the statistics of occupation of dislocation states taking into account the Coulomb interactions between accepted electrons.

The most dramatic effect of dislocations was on the recombination of excess charge carriers [12–17]. It was found that carrier lifetime was inversely proportional to dislocation density in various semiconductors. At that time the lifetime was a crucial parameter in the operation of bipolar transistors. So, it is not surprising that for a long time the recombination at dislocations attracted a great deal of attention from many researchers in various laboratories.

2. Basic findings

In the late 1960s several research groups in Europe undertook experiments on plastically deformed germanium. For instance, conductivity and Hall-effect measurements were performed by Willoughby [18] in London, van Weeren *et al* [19] in Amsterdam, Kryłow and Auleytner [20, 21] in Warsaw, Gondi and Cavallini [22] in Bologna. Much more detailed investigations were performed by Schröter and Labusch [23, 24] in Göttingen, who interpreted the results in terms of a one-dimensional energy band of dislocations. This was legitimated by the fact that a straight-line segment of a perfect dislocation should exhibit translational symmetry.

Later on, when use of computers entered widely into standard scientific practice, it became possible to calculate directly the band structure of a dislocation core using the tight-binding approximation. This was initiated by Jones [25] in Exeter and Marklund [26] in Ůmea (Sweden). Much earlier, Bonch-Bruevich [27] in Moscow and Güth [28] and Teichler [29] in Stuttgart developed approximate theories for dislocation band states.

It was also found that dislocations effectively scattered charge carriers in semiconductors. There are two reasons for that. One is the deformation potential due to the long-range distortion of the lattice around a dislocation line. The other is the electrostatic potential of a charged dislocation. Pödőr [30] in Budapest derived a formula for the charged-dislocation-limited carrier mobility, which later on appeared in handbooks on semiconductor physics. In turn, Kawamura [31] in Cologne was the first to pay attention to another possible source of carrier scattering: the change in lattice topology introduced by the presence of a dislocation.

Very soon, the interest in electron properties of dislocations also expanded to include semiconductor compounds. In 1957 Haasen [32] had already pointed out that in plastically bent InSb crystals two different kinds of 60° dislocation should be generated, depending on the direction of bending. Indeed, each extra lattice half-plane of an edge-component dislocation in $A^{III}B^{V}$ or $A^{II}B^{VI}$ compounds may terminate with a row of either A or B atoms.

In 1960 I became engaged in a study of the photoconductivity of plastically bent germanium. I measured a dependence of the photoconductance on the intensity of the illumination at liquid nitrogen temperature. I then used a set of fine metal nets to attenuate the light intensity. Surprisingly, when I exploited all the nets available in the laboratory, the photoconductance still remained measurable. Wishing to reduce the light intensity further, to complete the experiment, I improvised by using, in the place of the temporarily unavailable nets, a nylon stocking provided on the spot by a (female) member of staff in the laboratory. Thanks to this I have succeeded in finding that the steady-state concentration of photocarriers increased linearly with the logarithm of the light intensity for a wide range of illumination. This fact is nowadays exploited in the DLTS (deep-level transient spectroscopy) method to distinguish between localized and extended electron traps.

The strange behaviour of dislocations as recombination flaws results from their many-electron nature. The capture rate of electrons at a dislocation depends—due to the Coulomb interaction—on the number of electrons already captured [33–35]. This leads to a specific kinetics of recombination, in which excess carriers decay logarithmically with time; see figure 2.

Photoconductivity, as controlled by the generation–recombination processes, was more selective with respect to the dislocations than galvanomagnetic effects. Many investigators

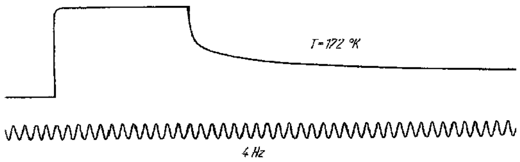

Figure 2. The logarithmic time decay of the photoconductivity in plastically bent germanium, after Jastrzebska and Figielski [35].

used it, together with recombination radiation, to get a deeper insight into the structure of dislocation electron states. Gołacki [36] in Warsaw was the first to reveal a complex spectrum of photoconductivity for plastically deformed germanium. This was next studied in more detail by Kamieniecki [37] in Warsaw, Kamieniecki and Elsässer [38] in Stuttgart, Weber [39] in Göttingen and Mergel and Labusch [40] in Clausthal.

3. Charge of dislocations and plasticity of semiconductors

Illumination changes the electric charge of dislocations in semiconductors. Hence, it was suspected from very early stages that mechanical properties of semiconductor crystals should also depend on the illumination.

In 1957 a discovery, known initially as the Kuczynski effect, fascinated solid-state scientists. Kuczynski and Hochman [41] at Notre Dame University (Indiana) studied microindentation of germanium and some other crystals using the diamond Knoop indenter. They noticed that illumination of the crystal during the indentation appreciably increased the longer diagonal of the impressed print. This meant that the microhardness of germanium decreased under illumination. Over a decade after this ‘discovery’, a lot of papers appeared in the literature, in which their authors reported on the observation of the Kuczynski (or photomechanical) effect and its very strange properties in various semiconductors and semimetals.

Finally, at the 9th International Conference on the Physics of Semiconductors, held in Moscow in 1968, the discovery was covered! That is, Hall [42] at General Electric, who performed similar experiments to those of Kuczynski, reported on his surprising result. The photomechanical effect was observed but only when the observer knew whether the light had been applied when each indentation was measured. Otherwise, the correlation between the illumination and print diagonal was purely statistical. But this was not the end of the story.

The next speaker at this conference was Juryi Osipyan [43] from Chernogolovka near Moscow. He presented stress–strain curves for CdS crystals, registered without any human interference, which displayed a pronounced effect of crystal hardening under illumination; see figure 3. Thus the photoplastic effect was supported by evidence, but not in elemental semiconductors, and with reversed sign. A great deal of effort has been made at the Institute of Solid State Physics in Chernogolovka, headed by Osipyan, to observe and understand this phenomenon, which occurs commonly in II–VI and III–V semiconductor compounds.

4. The issue becomes more complicated

Dangling bonds in a dislocation core are sources of uncompensated electron spins. They imply paramagnetic behaviour of dislocations. In fact, Alexander *et al* [44] in Cologne and Grazhulis *et al* [45] in Chernogolovka detected a complex electron-spin-resonance (ESR) spectrum

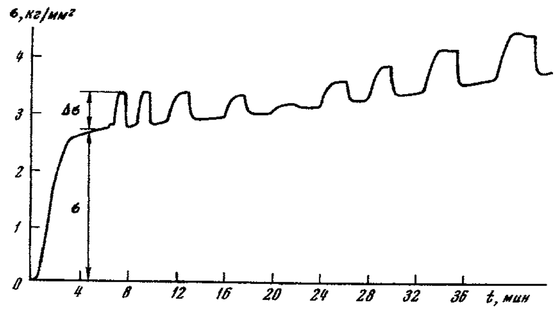

Figure 3. Photoplasticity of CdS at 75 °C, discovered by Osipyan and Savchenko [43]. The diagram shows the stress (in kg mm^{-2}) necessary to maintain a constant rate of compression of the sample, equal to 10^{-5} cm s^{-1}, as a function of the deformation time in minutes. Ranges of increased stress under illumination are apparent.

produced from plastically deformed silicon. It was next studied in much detail by Weber *et al* [46] in Cologne, who concluded that only a small fraction of all topologically possible dangling bonds at dislocations manifested themselves in the ESR spectrum. These paramagnetic centres must be located in very special dislocation segments. Instead, the majority of the dislocation core undergoes a reconstruction, in which the dangling bonds became saturated.

From this and other studies emerged a confusingly complex picture of the dislocation core in silicon and other semiconductors. It was compatible with a crucial discovery made in 1971 by Ray and Cockayne [47] in Oxford. They observed, with the help of the weak-beam method of electron microscopy, that dislocations in semiconductor crystals with tetrahedral coordination (to which group the diamond, sphalerite and wurtzite structures belong) were split into Shockley partials. The split segments, separated by stacking fault ribbon, were interrupted by short constrictions; see figure 4. The 60° dislocation splits into 30° and 90° partials, whereas the screw one splits into two 30° partials.

This finding brought about a small revolution in our understanding of dislocations in semiconductors. It showed that real dislocations in semiconductor crystals belonged mainly to the so-called glide system and not to the shuffle one as was believed earlier. For the glide system the glides of different parts of a crystal occur between closely spaced atoms on the $\{111\}$ planes. Thus, three times as many covalent bonds have to be broken as when the glides occur between widely spaced atomic planes. So, unexpectedly, the more realistic picture of the 60° dislocation appeared to be that shown in figure 5 and not the simple one shown in figure 1.

The complexity of the dislocation core and associated electron states was manifested also in photoluminescence originating at dislocations in silicon, observed for the first time by Drozdov *et al* [48] in Minsk (Belarus). In most semiconductors, dislocations act as killers of radiative recombination. A few semiconductors only—among them silicon and germanium [49]—exhibit optical emission due to dislocations. The emission spectrum of silicon consists of a number of sharp lines. The Cologne group attempted to correlate these lines with Shockley's partial dislocations split apart by different amounts.

By combination of the ESR method and photoconductivity, Wosiński [50] in Warsaw and Grazhulis *et al* [51] in Chernogolovka succeeded in observing an intriguing effect of spin-dependent recombination at dislocations in plastically deformed silicon. Moreover, Grazhulis *et al* [52] demonstrated also, with the help of ultrahigh-frequency experiments, the occurrence of ac conductivity along short regular segments of dislocations. This finding was next successfully applied in Chernogolovka to study dislocations in silicon.

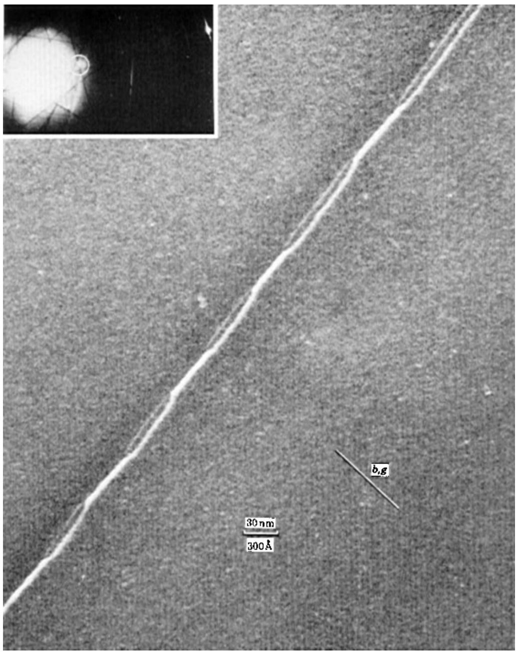

Figure 4. A weak-beam dark-field image of an annealed silicon specimen showing dissociated and constricted segments of a dislocation, taken from the original paper of Ray and Cockayne [47].

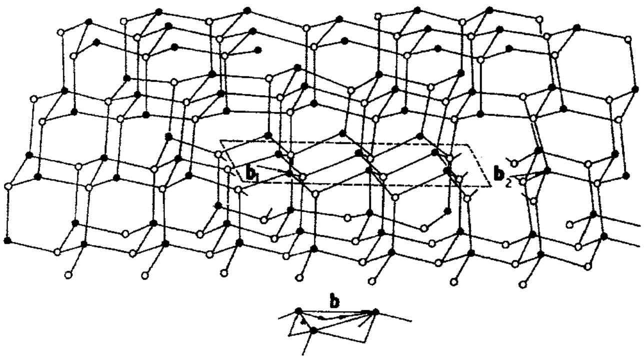

Figure 5. The 60° dislocation in diamond structure split into Shockley's partial dislocations: a 30° partial on the left and a 90° partial on the right, with a stacking fault in between marked by the dashed line (after Alexander *et al* [46]).

5. Final remarks

I have just come to the end of the story, as it was my intention to limit the scope of this outlook by stopping at the late 1970s. I think that the symposium on 'Dislocations in Tetrahedrally Coordinated Semiconductors' held in Hünfeld in 1978 is a good boundary marker. The great progress in the field which followed afterwards requires a separate treatment.

Here, at the very end, I want to add a few general remarks. Crystal dislocations are, on the one hand, detrimental defects of semiconductor materials and devices but, on the other hand, fascinating objects that draw the attention of many scientists from different branches of physics. There are some optimistic physicists, e.g. Mil'shtein [53], who helped to propagate the idea of exploiting directly specific electrical properties of dislocations in electronic circuitry. But it was also very soon recognized that dislocations in semiconductors represent interesting one-dimensional systems that might exhibit unusual electrical properties (this was long before the physics of low-dimensional systems aroused interest!)

Some physicists searched for one-dimensional dc conductivity and, what was much more attractive, for superconductivity along dislocation lines. A transition to the superconducting state could be induced by Peierls instability of a dislocation core. However, no definite indications of dc conductivity and superconductivity of dislocations have been established yet.

I also had dealings myself with a similar type of effect. I anticipated that an electric current induced in small prismatic loops in a semiconductor crystal could flow permanently at a sufficiently low temperature. I performed subtle experiments with specially prepared germanium crystals suspended on a fine quartz thread, which formed a torsion pendulum immersed in superfluid helium [54]. Unfortunately, the remanent magnetization of the samples made it impossible to verify the hypothesis.

Nowadays, we understand why dislocations represent rather bad one-dimensional systems. Dislocations, being line defects of the crystal lattice, themselves contain many inherent defects such as kinks, jogs and constrictions of dissociated segments, and are also decorated with impurities. All this disturbs the ideal periodicity along dislocation lines, which seems to be indispensable for the appearance of one-dimensional effects.

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