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100 YEARS OF SEMICONDUCTOR SCIENCE

THE UKRAINIAN CONTRIBUTION

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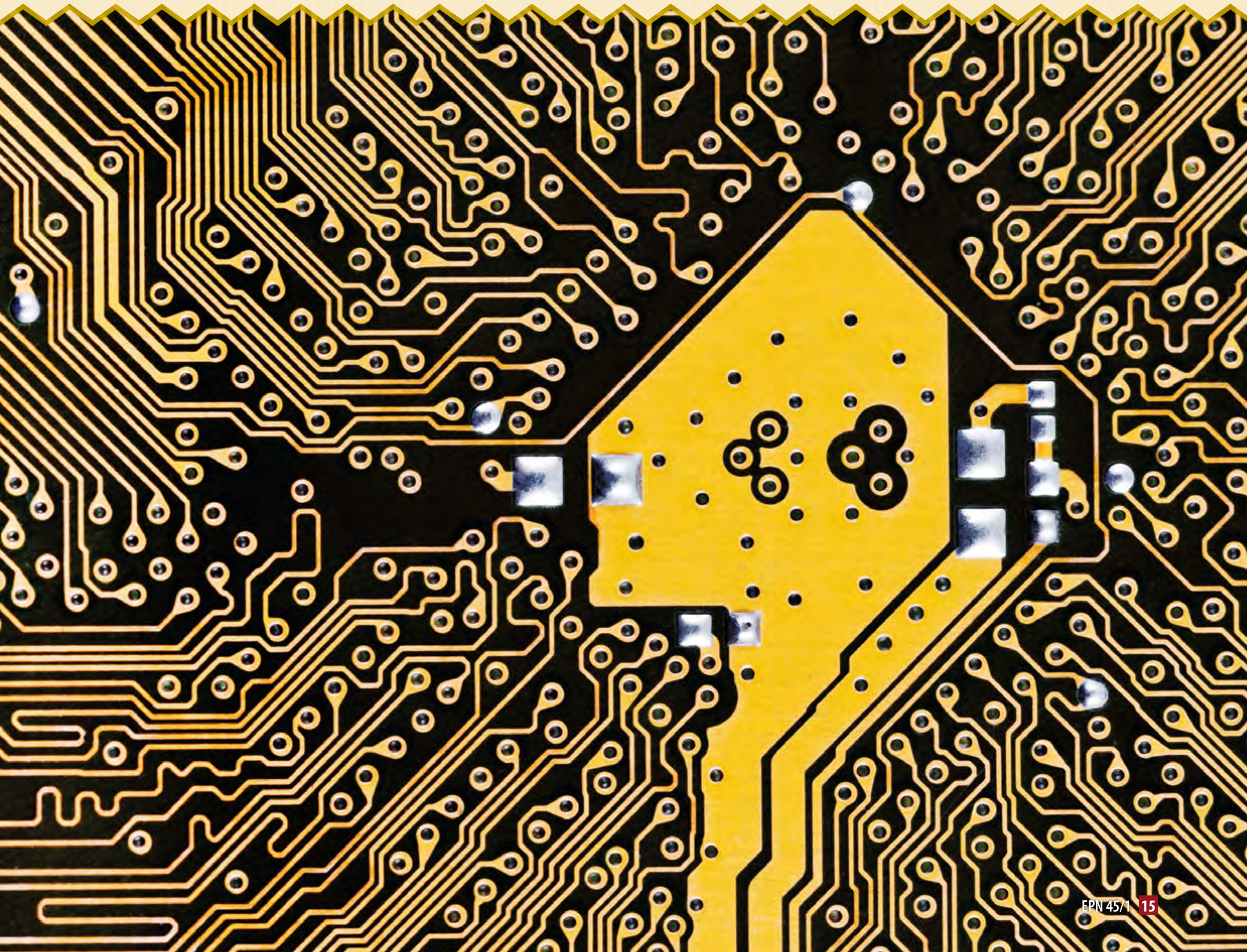
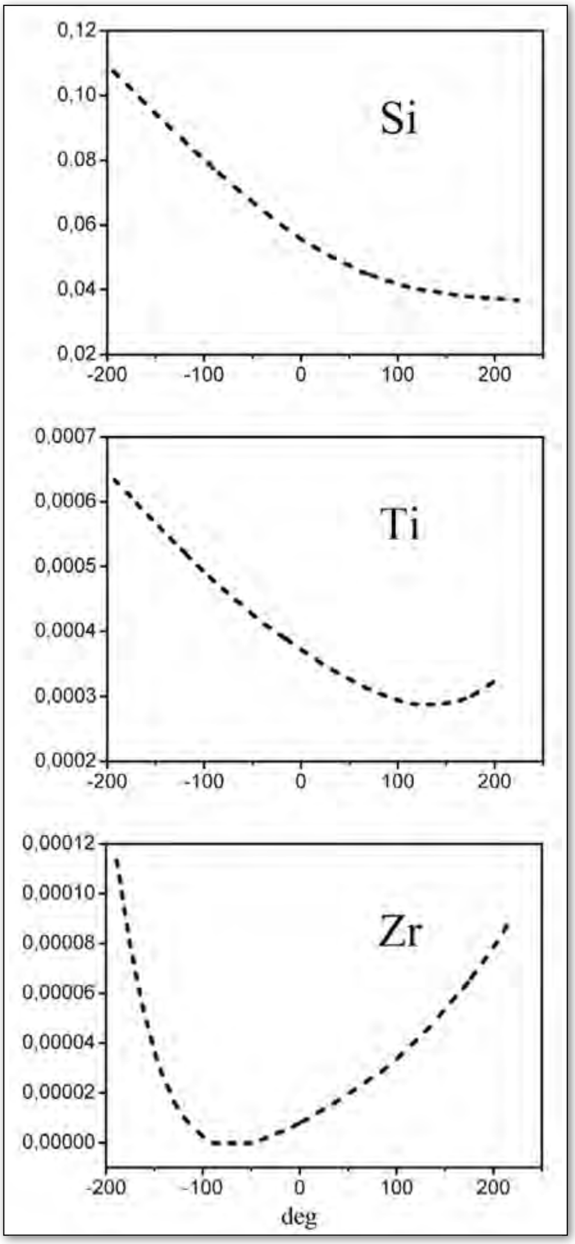
How old is semiconductor science? The answer is not obvious even for researchers who worked in this field for their whole life. Mankind has been dealing with semiconductors like silicon for centuries – although not with their electrical properties. The first electrical experiments with semiconductors were performed more than 200 years ago. However, the concept of semiconductors as a separate class of materials, between conductors and insulators, appeared rather late – in the first two decades of the 20th century.



In 1729 Stephen Gray (1679-1736) discovered the phenomenon of electro-conductivity: some materials (like metals, coal, human and animal tissues) were able to transfer electrical charge, while others (like rubber, silk, wax) were not. The reason for this difference was unclear.

The author of a rather informative study on the "early history" of semiconductors, Georg Busch [1], stresses that the first scientist to use the word "semiconductors" was Alessandro Volta (1745-1827), in his report to the London Royal Society in 1782. By touching a charged electrometer with different materials, he discovered that contact with metals caused immediate discharge of the electrometer. By contrast, contact with dielectrics caused no discharge at all. However, some materials ("semiconductors") caused discharge within a short but non-zero time. Later, in 1800, Volta constructed the first electric battery, which opened up a new field: the experimental study of electrical properties of different materials.

▸ FIG. 1: Temperature dependences of the resistivity of Si, Ti, Zr (data from [2]).



In 1821 Humphry Devy (1778-1829), using Volta's battery, discovered the increase in resistivity of metals with increasing temperature. However, in 1833 Michael Faraday (1791-1867) had observed the first exception: the resistivity of Ag_2S at room temperature was rather high, but at 175 °C it decreased rapidly to "metallic" values.

Later the effect of light on conductivity was discovered: in 1839 Edmond Becquerel (1820-1891) observed the photo-galvanic effect on a silver chloride plate with platinum contacts, placed in an electrolyte. In 1873 Willoughby Smith (1828-1891) observed a dramatic decrease in resistivity for selenium samples irradiation by light. A year later, in 1874, Karl Ferdinand Braun (1850-1918, Nobel prize in physics 1909) discovered the rectifying properties of a point contact between a metal and a metal sulfide. Although some of these effects were used almost immediately in technology (in exposure meters, radio receivers *etc.*) their physical nature remained unclear.

In 1897 Joseph John Thomson (1856-1940) had demonstrated that cathode rays consist of small charged particles – electrons. Thus the problem of charge carriers in conductors was solved. The basic concept of electrons was further worked out by Paul Drude (1863-1906) in his classical theory of the electrical conductivity of metals (1900). The reason for the resistivity increase with temperature became clear: the scattering of electrons becomes more intensive. Therefore, the resistivity of metals at high temperatures can be written as:

$$\rho(t) = \rho_0(1+\alpha t) \,, \qquad (1)$$

where t is temperature in °C, and α is a material constant. (Analytically, eq. (1) was obtained in the classical limit of high temperatures in the electron-phonon interaction scheme by Felix Bloch in 1930.)

Semiconductors as a separate class

Drude's theory could not explain the behavior of materials for which the resistivity *decreased* with temperature. The next step to explain this "anomaly" was made by Johann Koenigsberger (1874-1946), professor at Freiburg university in Germany. In [2] Koenigsberger and Shilling demonstrated that the temperature dependence of the resistivity of some materials (like titanium and zirconium) has a minimum, while for silicon the resistivity decreases in the whole temperature range under examination (fig.1).

In order to explain the observations, Koenigsberger had postulated that free electrons result from dissociation of atoms into mobile electrons and fixed ions. Consequently, the electron concentration N is given by:

$$N = N_0 \exp\left(-\frac{Q}{t+273}\right), \qquad (2)$$

where Q is proportional to the dissociation energy. This assumption allows one to rewrite (1) as:

$$\rho(t) = \rho_0(1+\alpha t)\exp\left(\frac{Q}{t+273}\right), \qquad (3)$$

which could obviously explain the minimum in the curves in fig.1! Although Koenigsberger could not propose any physical model for the origin of the dissociation energy, in his further work [3] he had divided all materials into metals, insulators and "variable conductors" (*variabele Leiter*) depending on the value of Q: for insulators Q is infinitely large (so there are no free electrons), while for metals at high temperatures it is zero (so the number of electrons in metals is equal to the number of ions – which was a basic assumption of Drude's theory). By contrast, the value of Q is finite in "variable conductors"; therefore their resistivity decreases exponentially with temperature.

Year of birth 1914

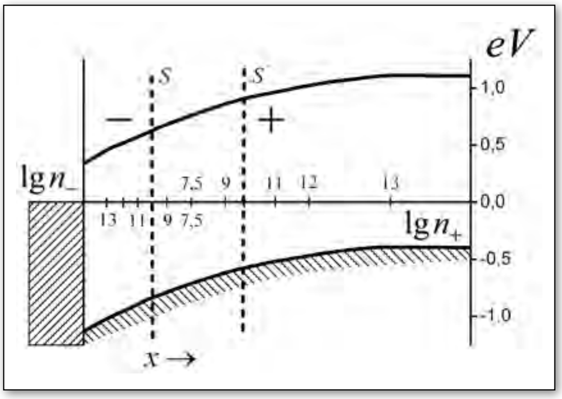
Note that Koenigsberger had also demonstrated experimentally that Q in "variable conductors" depends critically on their purity and the presence of defects. This allows us to coin the birth year of semiconductor science as 1914 – the time when [3] appeared, because since that time it was possible to speak about a new class of solids with strictly defined properties, rather than about some separate "anomalous" materials.

The band theory of semiconductors was developed by Alan Wilson (1906-1995) in 1931, soon after the basis of quantum mechanics was established. In two articles [4,5] he drew a picture of energy bands and energy gaps in between. Therefore, Koenigsberger's dissociation energy got a physical meaning as the gap between the upper band, completely occupied by electrons ('valence band'), and the next empty one ('conduction band'). Note that the concept of "holes" (carriers with positive charge, presenting unoccupied positions in the mainly occupied valence band) was introduced in the same year by Werner Heisenberg [6].

Although the basic features of semiconductor theory were developed in the 1930s, semiconductors remained "unpopular" until the mid 1940s for lack of suitable technologies. All crystals were "dirty", and results obtained were irreproducible. The situation changed after the fabrication of the first transistor on *p*-*n*-junctions (1951). William Shockley (1910-1989) together with his colleagues John Bardeen (1908-1991) and Walter Brattain (1902-1987) was awarded the Nobel Prize in physics 1956. The first chip including two transistors, resistor and several capacitors was fabricated from a 2 cm diameter silicon crystal in 1959. Very soon the use of semiconductor chips increased the possibilities of mankind dramatically. Semiconductors became a focal point for scientists and technologists all over the world.

P-*n*-junction: Ukrainian "origin"

The study of semiconductors started rather early in Ukraine. In 1929 the founder of the Institute of Physics of Ukrainian Academy of Sciences in Kyiv (Kiev), Oleksandr Goldman (1884-1971), began studying the Becquerel photo-galvanic effect. Unfortunately, Goldman, who was accused of being "Ukrainian nationalist" despite his Jewish origin, was arrested in the time of "great Terror" in 1938. Therefore he could renew his research activities only after returning from prison and exile many years later.



▲ **FIG. 2:** The first scheme of a *p*-*n*-junction (from [7]). The region of *p*-conductivity is at the right from vertical line *S'*, and the region of *n*-conductivity is left from *S*. The numbers along the horizontal axis denote the logarithm of hole (n_+) and electron (n_-) concentrations.

However, at least one of the greatest achievements of semiconductor science of the 20th century is connected with the Ukrainian capital Kyiv. Vadym Lashkaryov (1903-1974), after returning to Ukraine from his exile in northern Russia (he was accused of "contra-revolutionary activity" in 1935), became head of the semiconductors physics department in the Institute of Physics. There he developed the method of thermo-probe and applied it to investigate cuprous oxide and silver sulfide photocells, and selenium rectifiers. These experiments served to demonstrate the existence of *p*-*n*-junctions for the first time [7]. Fig. 2 shows the scheme of energies of the conduction band (upper graph) and valence band (lower graph) vs. coordinate in the *p*-*n*-junction of the rectifier or solar cell described in [7]. The role of *p*-*n*-junctions in photocells was studied as well.

"At least one of the greatest achievements of semiconductor science of the 20th century is connected with the Ukrainian capital"

Although the importance of this discovery for semiconductor physics can hardly be overestimated, reference [7] remains rather unknown in the West, and Russell Shoemaker Ohl (1898 - 1987) is generally recognized as being the first person to work with *p*-*n*-junctions [8]. As a matter of fact, however, Ohl's patent [9] was filed on May 27, 1941 (after Lashkaryov's paper [7] had already appeared), and was issued on June 25, 1946, whereas the earliest printed articles on p-n-junctions in germanium and lead sulfide appeared in the West in 1947 (see [10] and references therein). Therefore, the priority in this field obviously belongs to Lashkaryov's paper [7] which also demonstrates deep understanding of the physics of the phenomena being described.

After the second World War Vadym Lashkaryov established the Department of Semiconductor Physics of Kyiv University, and in 1960 the Institute of Semiconductor Physics of the Ukrainian Academy of Sciences, which now carries his name. A brief survey of the main results of semiconductor science in Ukraine, connected also with the names of Vasyl Liashenko and Oleh Snitko (surface science), Mykhajlo Lysytsia (semiconductor optics), Musij Sheinkman (recombination phenomena), Vitaliy Strikha (metal-semiconductor contacts, sensors), Solomon Pekar, Kyrylo Tolpygo and Kornij Tovstiuk (semiconductors theory), and many other prominent researchers, is presented in [11].

Semiconductor science, after reaching some stage of saturation, enjoyed a powerful impact from the development of nanotechnology, photovoltaics and graphene physics. Therefore the Ukrainian Physical Society proclaimed the hundredth anniversary of semiconductor physics in 2014 as the Year of Semiconductors in Ukraine in order to focus public attention onto research in this important field. ■

About the authors

Volod,ymyr Lytovchenko was born in 1931 in Kyiv (Kiev). After graduating in semiconductor physics in 1955, he joined the Institute of Physics, and since 1960 the Institute of Semiconductor Physics of the NAS of Ukraine. He is one of the founders of semiconductor surface physics and author of numerous effects (luminescence of semiconductor surface, 1974; defect-induced gap in ultrathin graphite-like films, 1988; etc). He served as president of the Ukrainian Physical Society in 2004-2013.

Maksym Strikha was born in 1961 in Kyiv (Kiev). After graduating in semiconductor physics in 1983, he joined the Institute of Semiconductor Physics of the NAS of Ukraine. His main research interests are in semiconductor theory and graphene physics. In 2008-2010 he was deputy minister of education and science of Ukraine. He is president of the Ukrainian Physical Society since 2013.

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▸ **FIG. 3:** Vadym Lashkaryov (seated, third from left) with his colleagues of the Department of Semiconductors Physics at Kyiv University (1956).