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Published monthly as twelve issues per annual volume by Institute of Physics Publishing Ltd, Techno House, Redcliffe Way, Bristol BS1 6NX. UK

Subscription information 1995 volume

For all countries except the United States, Canada and Mexico, the subscription rates are: institutions £85 per annum, individuals £34 in EC, £37 elsewhere per annum. Single issues £7.25. Orders to IOP Circulation Centre, WDIS, Publishing House, Victoria Road, Ruislip, Middlesex HA4 05X, UK (tel. +44 (0)181 845 8545; fax +44 (0)181 845 7696). For the United States, Canada and Mexico, the subscription rates are: institutions US\$ 160 per annum individuals US\$ 61 per annum. Orders to: American Institute of Physics, 500 Sunnyside Blvd, Woodbury, NY 11797, USA

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United States Postal Identification Statement

Physics World (ISSN 0953-8585) is published monthly for \$160 per year within the United States in association with the American Institute of Physics, 500 Sunnyside Blvd, Woodbury, NY 11797. Second class postage paid at Woodbury, NY and additional mailing offices.

POSTMASTER: Send address changes to *Physics World*, American Institute of Physics, 500 Sunnyside Blvd, Woodbury, NY 11797.

Bibliographic codes ISSN: 0953-8585 CODEN: PHWOEW Printed in the UK by Warners (Midlands) plc, The Maltings, West Street, Bourne, Lincolnshire PE10 9PH

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PHYSICS world

What future for X-rays?

Why is *Physics World* not celebrating the centenary of the discovery of X-rays? Surely the discovery that won the first Nobel Prize in Physics – a mere six years after Röntgen stunned the world with photographs of human bones and other "invisible" objects – should be feted in these pages. And it is certainly cause for celebration that, thanks to synchrotron radiation sources, the world now has a copious supply of X-ray photons for a wide range of experiments in physics, chemistry, biology, materials and beyond.

But it is also worth highlighting, as this issue does, the relentless increases in computer power made possible by advances in silicon technology, and the physics challenges facing that industry (pp15–16 and 29–51). Indeed the X-ray and silicon worlds already overlap: X-ray lithography is a possible replacement for optical/ultraviolet systems as the feature sizes in integrated circuits approach 0.1 µm. And silicon components are playing an important role in X-ray optics as scientists struggle to cope with the heat-loads associated with the brightest X-ray sources.

The silicon industry has a clear idea of where it has to go in the next few decades. What do we see if we gaze into an X-ray crystal ball? The traditional X-ray tube is now rarely used in research although at least one can be found in most airports, hospitals and dental surgeries. Synchrotron radiation sources obviously dominate the picture but the intense competition for beam-time means that there is also a demand for lab-sized sources.

Plasma-based sources look the most promising. A laser-produced plasma can generate X-rays in a variety of ways: it is possible, for example, to set up a population inversion – the main prerequisite for laser behaviour – at X-ray wavelengths in a plasma. However, the take-up of X-ray lasers has been slow, with applications largely limited to probing other laser-produced plasmas (e.g. in laser fusion experiments). Nonlinear processes such as harmonic generation – in which odd numbers of photons are bundled into a single photon with a proportionally shorter wavelength – are just beginning to access the X-ray region. As it becomes possible to pack more laser energy into shorter pulses, nonlinear effects will increase. Exotic schemes involving the damping of plasma waves could produce photons at hard X-ray wavelengths.

But the most promising of all the laser-plasma sources, from the applications point of view, are thermal plasmas. The black-body radiation from a million-degree plasma stretches into the X-ray region of the spectrum, and the strongest emission lines from the plasma are competitive with synchrotron sources in some types of experiment. Create a hundred of these mini-plasmas every second and you have a high-average-power source that can be used in lithography, microscopy and microfabrication. All you need is a table-top laser and a supply of low-Z material (such as the plastic on the back of audio cassette tapes!)

All these X-rays are of little use without the associated optics and detectors. The count rates in X-ray experiments are enormous, and expensive materials like diamond may have to be pressed into service to cope with them. And X-ray optics is notoriously difficult: ordinary mirrors don't work at normal incidence and give large aberrations that are hard to reduce when used at grazing incidence. Multilayers mirrors are used for near-normal incidence, but layers only a few atoms thick are needed, which leads to problems with interface roughness. Diffractive elements are best for high spatial resolution but currently have their own problems — mostly inefficiency.

One remarkable aspect of the discovery of X-rays was the speed with which applications emerged. If X-rays continue to infiltrate applications other than radiography and research – IC fabrication for example – the consequences could be just as important.



Silicides are a simple family of materials combining metal with silicon, but the latest generations of microchips have promoted these materials from the relative obscurity of inorganic chemistry to the forefront of semiconductor technology

Simply irresistible silicides

KAREN MAEX

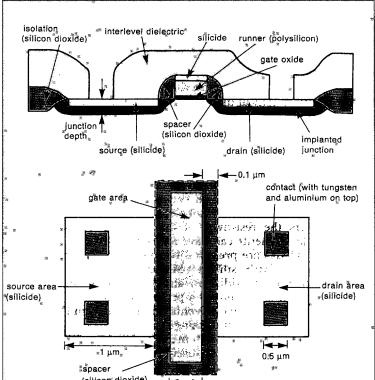
IF THE microelectronics industry is to continue to satisfy the demand for ever increasing amounts of memory from computers, it needs to manufacture devices on ever smaller scales. However, each new generation of logic chips depends on having materials with the right characteristics to make fabrication both economical and practical. In the latest generations of logic circuits, one group of materials, the silicides, has proved highly beneficial.

The growing interest in the application of silicides to microelectronics has widened the scope of silicide research and opened up many new avenues of investigation. The focal point of much of this work has been in improving our understanding of how silicides behave in combination with the other materials found in devices. No new material would ever be considered for device implementation unless industry was convinced that the material was compatible with current manufacturing processes and easily integrated into conventional integrated circuit (IC) technologies.

Almost all metals in the periodic table react with silicon to form silicides, which have the general chemical formula M_xSi_y. Most silicides are metallic, have low resistivity and can be divided into three main categories. There are the "refractory metal silicides", such as titanium silicide (TiSi2) and tungsten silicide (WSi), which generally have a high thermal stability; the "near-noble metal silicides", such as platinum silicide (PtSi) and cobalt silicide, whose main asset lies in their chemical reactivity; and the "rare earth metal silicides", like erbium silicide (ErSi2), which are mainly investigated for their optical properties, such as their ability to absorb infrared light. Although the process of forming a silicide, known as "silicidation", is complex, the material properties of silicides have been widely studied and extensive reviews are available (see Further reading).

One driving technology behind current and future developments in microelectronics is complementary metal oxide silicon (CMOS). CMOS circuits have main applications: memories and microproceschips connecting transistors and other devices together) are the important factors for microprocessors. In both cases, memory bits are interconnected with long, narrow conductors known as "word lines", and it turns out that interconnects made from silicides can speed up signal propagation times by lowering the electrical resistance of these lines. Indeed, a "polycide" technology, mainly based on WSi2, introduced into industrial production lines more

1 A metal oxide silicon field effect transistor (MOSFET) shown in cross-section (top) and viewed from above (bottom). Current flows from the source to the drain. The presence of the silicide helps to lower the resistance of the source and drain areas, a crucial factor in industry's quest to manufacture ever smaller devices. Typical dimensions are indicated for 0.25 µm fabrication technology.





than a decade ago, has improved propagation speeds by almost a factor of ten.

However, when industry started manufacturing the 0.5 µm generation of CMOS circuits about five years ago, it became clear that any further miniaturization would require technology changes to the transistor itself. This is where silicides have begun to play a key role. Figure 1 shows a schematic cross-section of a typical metal oxide semiconductor field effect transistor (MOSFET) for 0.25 µm technology. The critical dimensions are the gate length, which is used to define the "feature size" of the transistor quoted above, the depth of the p-n junctions forming the source and drain contacts, and the contact surfaces themselves. Electrical current mainly flows horizontally in the p-n junction of the contact, but the resistance to the flow of current depends on the crosssectional area of the junction and its intrinsic resistivity. Because of the limit to the number of dopants that can be solubilized in a given volume of silicon, there is also a limit to the intrinsic resistivity of the junction. The unfortunate consequence of this is that as the junction depth decreases, the total resistance of the contact goes up, jeopardizing the

The National Technology Roadmap for Semiconductors				
Feature size (µm)	Junction depth (µm)	Bits/chip (DRAM)	Bits/chip (SRAM)	Year of production
0.50	0.20	16 M	4 M	1992
0.35	0.15	64 M	16 M	1995
0.25	0.12	256 M	64 M	1998
0.18	0.10	1 G	256 M	2001
0.12	0.08	4 G	16	2004

As the memory requirement from computers continues to grow ever larger, each successive generation of logic circuits needs smaller and smaller features – including the p-n junction depth in transistors.

Source: Semiconductor Industries Association Roadmap (1994).

relative improvement of the device speed that one expects during scaling to smaller dimensions.

To illustrate this point, table 1 gives typical junction depths for various generations of logic circuits. The expectation is that as the feature size (i.e. the gate length) of circuits falls from today's 0.5 to 0.12 μ m by the year 2004, the junction depth will have to shrink from 0.2 to 0.08 μ m. In other words, as the gate length is scaled down, the other critical dimensions of the transistors have to be reduced to keep performance at an acceptable level.

It was to overcome these problems that many manufacturers began to introduce a silicide fabrication step into the production of the 0.5 μm generation of circuits. In this process, known as "self-aligned silicide" or "salicide", a silicide is simultaneously formed on the gate and source/drain areas through a reaction between the silicon and a metal, such as titanium or cobalt. The presence of the silicide lowers the resistivity of the junction. Although some metallic elements can have an even lower resistivity (figure 2), silicides are preferred because they form more stable contacts with silicon. Silicides also have the advantage that they oxidize in air, a process known as "self-passivation", to produce a protective silicon dioxide (SiO₂) surface barrier that prevents the silicide from being attacked during further processing.

The lack of reactivity between metal and SiO_2 is a crucial factor because SiO_2 is also used as a dielectric layer isolating one component from the other. In addition, it bestows the unique property of self-alignment. This is a

best self-aligning properties are PtSi, NiSi, CoSi₂ and TiSi₂ because their reaction with silicon is the most controllable. PtSi has been used extensively in bipolar and infrared detector applications. Unfortunately it has poor thermal stability and is not the ideal choice for a CMOS circuit. NiSi has also been investigated in detail, but it is unstable in contact with silicon. TiSi₂ and CoSi₂ are therefore the two main silicides that have been of interest to MOS technology. TiSi₂ is now widely accepted by integrated circuit manufacturers, but recent studies have shown that CoSi₂ has even better properties and could also be considered a serious candidate.

Hot stuff

What happens when a metal reacts with silicon to form a silicide? In the case of titanium or cobalt, experiments on bulk reactants have given us a fairly good empirical idea of what is going on. However, we need to know what happens when a thin film of the metal reacts with the silicon. This type of system is a long way from thermodynamic equilibrium because the reaction takes place in the solid state at temperatures between 500 °C and 800 °C. Under these conditions the elements are able to diffuse, and the system can lower its free energy by forming a series of different intermetallic phases.

The so-called "phase formation sequence" in the reaction between thin metal films and silicon has been investigated extensively since the late 1960s by F M d'Heurle at the IBM Yorktown Heights Laboratory in New York, M-A Nicolet at California Institute of Tech-

nology in Pasadena and J Mayer at Cornell University, among many others. It turns out that the presence of small amounts of contaminants, such as oxygen or carbon – either in the metal or at the metal/silicon interface – have a big impact on the solid-state reaction. However, if the reaction occurs in a well controlled environment, as is mandatory for microelectronic processes, the phase sequences shown in figure 3 are observed for the cobalt/silicon and the titanium/silicon reactions.

The reaction of a thin cobalt film with silicon was worked out theoretically by Ulrich Gösele and King Ning Tu back in 1982. The cobalt diffuses into the silicon to form a cobalt-rich (Co₂Si) phase (figure 3a). This then turns into the monosilicide CoSi. Finally, when there is no free cobalt left, nucleation of CoSi₂ begins.

For silicidation of titanium a different process takes place. Here the TiSi₂ phase forms immediately. However, there are two allotropic TiSi₂ phases, each with a different orthorhombic crystal structure (figure 3b). One phase, referred to as C49, is full of defects and forms at temperatures below 600° C. The

2 The specific resistivity of various silicides and some metals. In comparison, the specific resistivity of highly doped silicon is

~ 500 μΩ cm.

100

MoSi₂

WSi₂

NiSi₂

TaSi₂

Ti

TiSi₂

CoSi₂

NiSi

W Mo



lower resistivity (figure 2).

In both cases, however, the silicide phase that ends up in thermal equilibrium with the silicon is the one with the lowest electrical resistivity. Because the solid solubility of titanium and cobalt in silicon is extremely low, titanium and cobalt impurities in silicon do not interfere with the almost ideal semiconducting properties of silicon.

Although the reaction between metal and silicon is important, so is the possibility of an interaction between the metal and any remaining SiO₂ on the surface of the silicon that has not been properly removed. Cobalt has no significant interaction with SiO₂ but titanium can reduce SiO₂, because of its high reactivity with oxygen. Thus, when titanium is deposited on the surface of the silicon

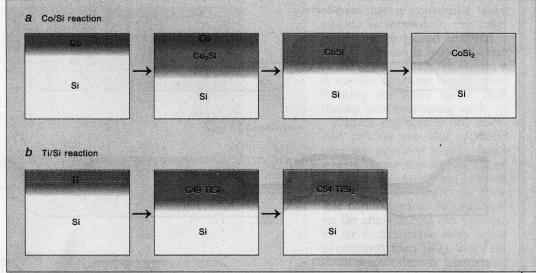
it is less critical for the surface to be perfectly clean. This has practical advantages because surface-cleaning procedures, which are still somewhat problematic and poorly controlled, do not have to be so stringent in this case.

Silicides in runners and gates

Ultralarge-scale integration (ULSI) is a term used to describe the grouping of many electronic components in the form of large and complex integrated circuits onto a single chip. In these circuits the gate electrode and the local electrical connections consist of very narrow lines of silicon in polycrystalline form, known as "polysilicon". Surrounding these lines are areas of SiO₂ (figure 4a). When such circuits are manufactured, a layer of metal is deposited onto each transistor (figure 4b). The idea is for the metal to react with the polysilicon, converting it into a silicide, but not with the SiO₂ (figure 4c). Because the silicide should not form in surrounding regions, the reaction is said to be "laterally confined".

Although lateral confinement does not fundamentally change the reaction kinetics, these new boundary conditions may influence the rate at which the silicide lines are formed. This is particularly so for TiSi₂. Here, the C49– C54 transition between the two different allotropic forms of TiSi₂, which normally takes place at above 600 °C, is actually slowed down on these narrow polysilicon lines because of a lack of nucleation centres. However, the transition can be accelerated using rapid thermal processing. In this technique a single wafer is heated by radiation from a lamp to around 800 °C for a couple of seconds. The higher temperature helps to yield more nucleation sites for the C54 phase and the short reaction time postpones the disintegration of the silicide film. For CoSi₂, however, these nucleation problems are not encountered: the CoSi-CoSi2 transformation (the final step in figure 3a) occurs faster in thinner films than in the thicker ones.

The thermal stability of thin silicide films on silicon is a major concern, since it limits the "thermal budget" allowed



3 Thin films of cobalt or titanium can form silicides by reacting with silicon. The reaction takes place in the solid state at temperatures of 500-800 °C, with each stage typically lasting 30 s. In both cases, various phases are encountered. (a) Cobalt first diffuses into the silicon to form a cobalt-rich (Co_2Si) phase. This then turns into CoSi. Finally, when there is no more free cobalt left, $CoSi_2$ starts to form. (b) The silicidation of titanium is different. The $TiSi_2$ phase forms immediately and there are two allotropic $TiSi_2$ phases – C49 and C54 – each of which has its own orthorhombic crystal structure.

reactions as fast and at as low a temperature as possible. Overexpose the wafer to heat, and the microstructure can fall apart through processes such as "grooving" and "islanding". Both CoSi₂ and TiSi₂ are polycrystalline and suffer from these problems during prolonged high-temperature treatments. Thermal grooving is influenced by both thermodynamic and kinetic factors. From a thermodynamic point of view, the driving force for the morphological transformation is the reduction of the interface/surface energies. The grooving process occurs because of local energy equilibrium at the intersection of a grain boundary and the film surface or interface, causing matter to diffuse away from the grain edges.

Doping contacts

The creation of a silicide on the source and drain regions in a MOS transistor reduces the total resistance to the current flow. This resistance consists of two parts: the intrinsic resistance in the channel region, which depends on the voltage applied to the gate, and the series resistance of the source—drain contacts between the doped junction and the metal that is used to wire all of the transistors together, which is independent of the applied bias. The contact between the wiring metal (through the silicide) and the silicon is said to be "ohmic" and its formation requires the silicon to be doped.

Typical dopants in silicon include arsenic and phosphorus as electron donors and boron as electron acceptors. Because these dopant elements are able to diffuse, they play an active role in the silicidation reaction. Since silicide films are polycrystalline, the diffusion of these dopants depends on the sum of two separate factors: diffusion in the bulk lattice and (much faster) along the grain boundary.

For a TiSi₂ film on the source or drain of a transistor, the diffusion of dopants can even lead to the formation of titanium/dopant compounds. This consumes most of the dopants, reducing the doping level at the interface between the silicide and the silicon. Since the concentration of



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