Structural Properties of Silicides and Silicide - Silicon Interfaces: Transmission Electron Microscopy

Helmut Föll

Siemens AG, Otto-Hahn-Ring 6,
8000 Muenchen 83, West-Germany

Tung-Shen Kuan

IBM, T.J. Watson Research Center,
P.O. Box 218, Yorktown Heigths,
N.Y. 10598, U.S.A.

1. Introduction

In a recent review paper about depth-profiling techniques /   /, Mayer and Poate stated that "characterization of thin film interdiffusion and interfacial reactions poses a nearly impossible question: how does one analyze a layer 10 to 100 atoms in thickness (or less) that is located some 1000 or 10000 atom layers below the surface". The authors proceeded by discussing several techniques capable of analyzing thin layers - most notably Rutherford backscattering and depth-profiling by sputter methods. They did not mention transmission electron microscopy (TEM) although TEM in connection with cross-sectional specimens is easily capable of delivering structural and analytical information on the scale requested. The apparent neglect of TEM in /   /, however, was not due to an oversight of the authors but simply to the circumstance that before 1978 hardly any TEM work had been performed with silicides or similar multi-layered structures. Since then the vast potential of TEM for the study of structural properties of silicides and silicide-silicon interfaces has been realized and this is documented in the rapidly increasing number of silicide papers that include TEM work.

TEM is the only method capable of delivering local information about the microstructure and, in the analytical mode, composition of silicides and interfaces. Other techniques as, e.g., Rutherford backscattering, are averaging techniques over areas in the mm^2 region. This may lead to problems if the structure investigated is not very homogeneous. A non-flat, but sharp interface (as, e.g. the Si-$NiSi_2$ interface in Fig.   ) would appear to be smeared-out in any averaging technique.

All the instrumentation and the techniques needed for high-powered TEM work have been available for several years. The technique of preparing cross-sectional specimens is known since 1969 /   / and high-resolution microscopes also have been available for many years. What prevented TEM from being exploited for silicide research much earlier were, in our opinion, the intricacies of specimen preparation, microscope operation and image interpretation. Whereas it is still true that many applications of TEM do require skilled experimental work and rather involved contrast theories, it is often overlooked that an impressive amount of structural (and, to a certain degree, analytical) information can be obtained quickly and easily by utilizing well-established experimental techniques and image interpretation rules in connection with easy-to-operate, highly automated electron microscopes.

This paper intends to familiarize the reader with the potential and the limitations of TEM with respect to silicide research. Both well-established routine practices and state-of-the-art efforts will be presented and illustrated with examples from the work of the authors. Because most workers in the field are not familiar with contrast theories, a short chapter will introduce the essentials of contrast interpretation and special emphasis will be put on the presently maturing theory of high-resolution imaging. Then we will illustrate the application of TEM to silicides by discussing in some detail recent TEM studies of various silicides. A chapter about high-resolution TEM will follow and finally we will touch upon the structure of defects in epitaxial Si-silicide interfaces and their appearance on high-resolution micrographs.

2. The Instrument

2.1. Transmission Microscopes

In the beginning there were only transmission electron microscopes, customarily abbreviated by "TEM". It should be noted, however, that most abbreviations are used not only for the instrument, but also for its application, e.g. TEM for transmission electron microscopy. Nowadays many kinds of electron microscopes have emerged and the number of abbreviations is flourishing. A basic distinction can be made between direct-imaging microscopes and scanning microscopes. We will not attempt to give a complete zoology of electron microscopes but only to provide an overview of some important developments.

All direct-imaging microscopes pass a well-focussed, monochromatic and rather coherent electron-beam through a thin sample. With the aid of magnetic lenses the intensity- or phase-distribution of the electron waves emerging from the sample can be imaged onto a viewing screen or on a photographic plate with magnifications typically between 1000x and 500000x. The basic principle is known from numerous monographs / / and shall not be discussed in this paper. All direct imaging machines are TEM's and two groups of instruments have emerged, distiguished by their acceleration voltage for the electron-beam. "Conventional" TEM's operate at voltages between 100 kV and 200 kV, whereas "high-voltage electron microscopes", abbreviated HVEM, use voltages from 500 kV to 3 kV.

So far, HVEM's have not been utilized for silicide research because they are almost prohibitively expensive and difficult to operate, but they could offer advantages not obtainable with conventional TEM's / /. Much thicker specimens could be investigated and, since the high-energy electrons produce vacancies and interstitials in Si (and probably also in the silicide), it is conceivable that silicide-forming reactions could be induced and observed in-situ.

Other abbreviations frequently encountered are HREM = high-resolution microscopy and XTEM = TEM with cross-sectional specimens. CTEM = conventional TEM is used to distinguish conventional imaging methods from HREM or to draw a line to HVEM.

2.2. Scanning Microscopes

Scanning microscopy techniques and instruments have experienced a breathtaking development during the last ten years. Generally speaking, a finely focussed electron beam (focus size 0.2 nm) is scanned across the specimen. The interaction between the electron beam and the specimen produces a number of detectable physical phenomena which carry information about various properties of the sample. Massive samples can be used and in the best-known cases an image may be formed using secondary or back-scattered electrons in order to observe the surface topography (SEM = scanning electron microscopy); Auger electrons, carrying information about the presence and distribution of light elements (SAM = scanning Auger microscopy) or X-rays, providing information about the presence and distribution of heavier elements ("microprobe").

If thin samples are provided, a scanning electron microscope may also be used in transmission. With such a STEM (= scanning transmission electron microscope), an image of the sample essentially identical to that of a TEM can be produced /   /. In addition, analytical capabilities are usually provided in commercial STEM equipment. Most prominent is electron energy-loss spectroscopy /   / and X-ray spectroscopy; allowing the detection of light or heavy elements, respectively. The outstanding feature of STEM in the analytical mode is that a chemical analysis can be performed on a 1 nm scale /   /.

Whereas SEM and microprobe facilities have been extensively used in silicide research, most other techniques have been applied only sparingly or not at all. Especially STEM in the analytical mode would be perfectly suited to silicide research and we will present examples for its possible use. The bulk of the paper, however, will be concerned with TEM.

3. The Specimen

3.1. General Requirements

It is a wide-spread misconception that actual TEM work consists mainly of operating a microscope and taking photographs. In reality, the preparation of suitable specimens and the interpretation of the micrographs obtained frequently constitute the lions share of TEM efforts. Specimen preparation and image interpretation have to be considered an integral part of TEM and will be discussed accordingly.

Every TEM specimen has to meet very stringent requirements: It has to fit into a specimen holder allowing specimens at most 3 mm in diameter; it has to be very thin; it should have smooth and clean surfaces; it should not be bent or deformed; and it should not have changed in any way by the preparation procedure; i.e. it should be free of artifacts.

The small dimensions are a direct consequence of technical problems associated with the construction of magnetic lenses. High-resolution lenses, i.e. lenses with small abberration coefficients, can only be made with rather small openings in the ferro-magnetic pole-pieces and thus can accept only small specimens.

The specimen thickness is limited because the electrons must be able to pass through the specimen without excessive energy-losses; i.e. without much inelastic scattering. Energy losses change the wavelength of the electron-waves and, due to chromatic abberrations of the lenses, reduce the resolution. The maximum tolerable thickness of a specimen therefore depends on the resolution required. If only the mere detection of lattice defects like dislocation or stacking faults is required without any attention to their structural details, a Si specimen may be about 1 µm thick for 100 kV electrons and about 8 µm for 1 MeV electrons. Alternatively, if maximum resolution on an atomic scale is demanded, the maximum thickness of a Si sample is about 40 nm at 100 kV; for heavier elements it would be even smaller.

With respect to silicides it is meaningful to distinguish between two basically different kinds of specimen: "conventional" and "cross-sectional" specimens. The preparation of conventional specimens will be discussed first.

3.2. Preparation of Conventional Specimens

Fig. shows a typical preparation sequence. Firstly a specimen of suitable size is cut from the sample. For Si (with or without a silicide layer), this can be done by scribing and cleaving, but cutting with diamond- or wire-saws as well as drilling, can also be used. If the sample is rather thick (say more than 0.3mm); it may be pre-thinned by grinding using diamond or SiC slurry. The major step involves the final thinning from the backside. This can be done chemically or electro-chemically, or alternatively by ion-beam milling. Usually the thinning process is continued until a hole appears in the specimen. The edges of the hole then are mostly thin enough to allow TEM work. If the etchant does not attack the silicide,one may also obtain a sample with the silicide layer still intact, but with the Si completely removed. Chemical methods are quick and easy and a wealth of recipes for all kinds of specimens are reported in the literature (cf., e.g.

Major problems in preparing conventional specimens may result from excessive bending of the silicide layer due to stress relief as soon as a hole is formed or even complete peeling of the silicide due to corrosive reactions at the interface. Of course, interface-related structures as, e.g., voids in the interface or misfit dislocations can only be observed in samples where thin regions of the Si substrate are still present.

If chemical thinning cannot deliver the desired specimens, ion-milling has to be applied. This may be necessary, e.g., if the silicide film is very thick and no chemical method can be found that allows controlled thinning.

Ion-beam milling machines thin the sample by bombarding it with an Ar-ion beam of 500 V - 5000 V in energy that hits the sample under a shallow angle. Milling rates of several μm/hr are achievable; the preparation of a sample thus requires from a few hours up to a day of continued milling. Ion-milling has the basic advantage that it works for all samples regardless of their chemical nature or composition. The thinning-process is straightforward and does not require any material-specific knowledge or skills. Ion-milling also allows to removal of very small quantities of material in a controlled fashion and thus facilitates to locate the electron-transparent thin area precisely where it is supposed to be.

No light without shadows - ion-milling suffers serious disadvantages, too. First of all, it is a rather violent process that may introduce defects into the sample or, possibly, even induce chemical reactions / /. Secondly, the sample always heats up if no special care is taken and may assume temperature of a few 100 °C. Whenever ion-milled samples are investigated, the experimentalist has to be very wary of artifacts that may have been introduced.

3.3. Preparation of Cross-Sectional Samples

Cross-sectional samples literally add a new dimension to TEM investigations of layered structures but their preparation is considerably more involved than that of conventional specimens. Fig. illustrates a typical preparation sequence; more details can be found in / /. Assuming that a silicide-covered Si wafer is given, in a first step slabs of 2 x 6 mm in size are cut from the wafer. Several of those slabs (about 4-8) are glued together using a suitable epoxy. This is the critical step. The epoxy layer should be only about 1 µm thick (to avoid problems during ion-milling); but must have good adherence to the samples and enough strength to insure the integrity of the final sample. In order to achieve consistently good results it is advisable to keep the stack of specimens under pressure in a teflon-lined press during the curing of the epoxy. After the epoxy has hardened, the specimen-stack is cut into small platelets using a diamond- or string-saw. The platelets are ground to a final thickness of 50 µm; taking proper care to avoid cracking. The thin platelet then is glued to a support-ring and finally ion-milled until a hole appears at one of the junctions. This often involves proper adjustment of the milling conditions, otherwise the area of interest might be milled out completely long before the rest of the specimen is thin enough or, alternatively, all of the specimen has been milled away except for the junctions as shown in Fig.

Ion-milling, of course, is the only suitable way for thinning a cross-sectional specimen and one has to live with its shortcomings. In practice, finished specimens may have only very small electron-transparent areas at the interfaces and several attempts may be necessary before a suitable sample is obtained. Even more care is needed if a rather small silicide-covered area (i.e. a contact rectangle) is to be viewed in cross-section. The rewards, however, are well worth the effort and several laboratories have developed standard procedures for preparing cross-sectional specimens from almost any sample. In the Siemens labs, e.g., any given feature in a normal integrated circuit (no special test-structure) may be viewed in cross-section / / and Fig. gives an example of a silicide contact used in an commercially sold integrated circuit.

3.4. Concluding Remarks

The small size of the electron-transparent area of typical TEM specimens necessitates some restraint in judging the statistical significance of the data obtained. In an extreme case, a HREM micrograph may cover an area of about 70 x 100 mm² and this represents only about $3 \cdot 10^{-9}$ % of the area of a 2" wafer. Generally speaking, a conventional sample may have an electron-transparent area of 10^5 µm², whereas a cross-sectional sample offers only about 5 µm². It is therefore advisable to confirm one's findings by investigating several specimens prepared from different macroscopic samples.

A peculiar problem unique to cross-sectional samples finally merits to be mentioned: "artifacts" produced during printing the photographic negative. In most cases the silicide layer will appear much darker on a print because of the larger scattering-factors of the metal atoms as compared to Si. This difference in background contrast may not be too large for a photographic negative but often cannot be accommodated by photographic paper. Consequently, while printing a negative, some dodging might be needed which automatically leads to artificial contrast gradients right at the interface.

This may appear as blurred dark or bright areas at the interface and should not be confused with real interface contrast effects.

4. Imaging Techniques and Contrast Theory

4.1. General Remarks and Electron Diffraction

A thorough understanding of the mechanisms leading to a detectable contrast constitutes the key to all but the most simple TEM applications. Within the framework of this paper it is neither possible nor necessary to delve into the intricacies of contrast theory; for this the reader is referred to the numerous monographs in this field, cf. e.g. / /. A generalized and simplified overview, however, is indispensable for the understanding of what follows and for a general appreciation of the possibilities of TEM.

Three qualitatively different kinds of contrast-generating mechanisms may be distinguished: Mass-contrast, diffraction contrast, and phase contrast. These contrast-mechanisms are most easily discussed by reference to the electron-scattering or diffraction properties of a sample, i.e. in Fourier-space. Therefore the formation of diffraction patterns will be discussed first.

When a coherent electron-wave passes through a sample, parts of it will be scattered by the atoms via elastic or inelastic scattering events. The scattered intensity as a function of the scattering angle constitutes the diffraction pattern. Ideally, the diffraction pattern is the Fourier-transform of the spatial distribution of the scattering potentials (the atom) and, according to general laws of optics, an image of the diffraction pattern is formed in the back-focal plane of the objective lens. Every TEM can be switched into the "diffraction mode" in which it images the diffraction pattern onto the viewing screen. Fig. shows examples of typical diffraction patterns formed by an amorphous, a poly-crystalline, and a single-crystalline specimen. The area of the sample from which the diffraction pattern is taken can be as small as $1 \times 1\ \mu m^2$ in standard TEM's ("selected area diffraction" ability) or even smaller if a STEM is used ("micro-diffraction"). The rings (which are known as Debye-Scherrer rings) or dots in Fig. are formed in the common way by constructive interference between the electron waves scattered from atoms belonging to a particular set of lattice planes hkl which fulfill the Bragg-condition

$$= 2d_{hkl} \cdot \sin\Theta \qquad (1)$$

with = wave-length of the electrons; d_{hkl} = spacing of the hkl planes, and Θ = angle between hkl plane and electron-beam. Since is very small (0.0037 nm at 100 kV), Θ is small too (1°), and in a slightly simplified picture it may be said that all lattice planes approximately parallel to the electron-beam will be in a strongly diffracting position.

The distance R of a spot in the diffraction pattern and the central beam (also called zero-order beam, 000 -beam or transmitted beam) is given by

$$R = \frac{\cdot L}{d_{hkl}} \qquad (2)$$

with L being a geometric constant. The product ·L is called the camera-constant of the microscope and generally known or easily determined.

A diffraction pattern, once obtained, thus allows a quick and rather simple determination of the lattice parameters of an unknown substance and therewith usually an identification of the substance.

If the microscope is used in the imaging mode, an adjustable aperture is inserted in the back-focal plane; i.e. in the image plane of the diffraction pattern, allowing only some of the electrons forming the diffraction pattern to contribute to the image. In the bright-field mode, the aperture is placed over the central beam, excluding all scattered electrons from image formation. In the dark-field mode the aperture is placed somewhere else, e.g.

over a diffraction spot (after tilting the electron-beam so that the selected diffracted beam runs through the optical axis of the TEM).

4.2. Mass Contrast

Mass contrast can be understood most easily by considering an amorphous specimen. If only non-scattered electrons are admitted for image formation (bright-field mode), the image will be dark in regions from which many electrons have been scattered; e.g. in thick regions or in regions that contain a more strongly scattering atomic species. Alternatively, it will be bright in thin regions or regions containing holes or weakly scattering atoms. This is schematically illustrated in Fig. . It should be emphasized that mass contrast is not absorption contrast. TEM specimens are always so thin that electrons are never absorbed; even inelastic scattering can often be neglected.

If the specimen is crystalline, mass-contrast may be overwhelmed by diffraction effects. In order to observe mass-contrast it is necessary that no low-indexed lattice planes are strongly diffracting and that can be done by tilting the specimen into a suitable position with the aid of the goniometer stage always provided in TEM's. This is illustrated in Fig. where the same specimen area is imaged with predominantly mass-contrast or diffraction contrast, respectively. The specimen consists of a $NiSi_2$-layer on 100 Si and the mass-contrast is mostly due to the strongly scattering Ni atoms. It is obvious that the silicide thickness is rather non-uniform and that the silicide-Si interface is facetted. Mass contrast also is very useful with cross-sectional specimens. Because of the usually pronounced change in scattering potentials of Si and silicides, a sharp contrast step precisely defines the interface morphology.

4.3. Diffraction Contrast

Diffraction contrast is observed if at least one strongly diffracted beam is present. This can be achieved quite easily by tilting the specimen into a suitable orientation. Usually a position is chosen where only one strongly diffracted beam is excited; this is called a two-beam case and characterized by the diffraction vector g and the excitation error s. The diffraction vector is the reciprocal lattice vector characteristic for the set of lattice planes hkl ; it is usually drawn into a micrograph. The excitation error is a measure of the deviation of the angle θ between electron beam and the lattice planes from the Bragg-angle θ_B. For infinitesimaly thick specimens the diffracted beam would only have a finite intensity for $\theta = \theta_B$; i.e. for $s = 0$. For thin foils, however, the intensity of the diffracted beam decreases rapidly with $\theta_B - \theta$ but is finite, and strong diffracted beams are still obtained for s 0. This is the key to the imaging of all defects that possess a strain-field. Fig. demonstrates schematically the contrast generation at a dislocation by showing a cross-sectional view through a specimen containing two edge dislocations. The indicated lattice planes are close to, but not precisely at the Bragg-angle. Therefore not much intensity is scattered out of the transmitted beam and in the bright-field imaging mode the background intensity is high. On one side of one dislocation, however, the lattice planes are locally rotated closer to the exact Bragg angle. In these areas the diffracted beam is strong and the transmitted beam correspondingly weak. One dislocation therefore appears as a dark line whereas the other one does not produce any visible contrast. Obviously, dislocations are only visible if their strain-field has a substantial component perpendicular to the diffracting lattice planes; i.e. parallel to $\underline{g}$. This usually is not the case if $\underline{g}\cdot\underline{b} = 0$ and that is the common rule for the invisibility of dislocations which allows an analysis of their Burgers vector. Fig. shows that dislocations are present in the $NiSi_2$-Si specimen as will be discussed in detail in chapter 6.

If the specimen is bent dark lines will appear wherever the Bragg-condition is fulfilled; forming a system of bend-contours.

The width of the dislocation contrast profile depends on the extent to which the dislocation strain-field influences the diffraction properties. With normal bright-field conditions, the contrast width will be in the order of 10 nm. Thus, even though the resolution of the microscope may be 0.2 nm, the resolution limit for defects like dislocations is around 20 nm if no special techniques are used. One possibility to overcome that problem would be to work with very large excitation errors. Then only the most heavily bent lattice planes close to the dislocation core would be strongly diffracting and the image width would be small. Unfortunately the contrast decreases with decreasing contrast width and the image of the dislocations starts to fade out. A high contrast with small contrast-width can be achieved in the dark-field mode, however. Then the background contrast is essentially zero and the dislocation line appears as a narrow bright line. This is the so-called weak-beam technique /   / which allows to stretch the resolution limits for diffraction contrast to   2 nm.

So far we have not dealt with dynamical contrast effects. These arise from the re-diffraction of an already diffracted beam back to the zero-order beam. This always happens for small excitation errors, i.e., with strongly excited diffracted beams. The intensity then oscillates between the main beam and the diffracted beam as the electrons pass through the specimen; the wavelength of this oscillations is called extinction distance. An immediate consequence is that a wedge-shaped specimen will display a succession of bright and dark fringes outlining regions of constant thickness; so-called thickness fringes. If the specimen contains an inclined inner surface, e.g. a stacking-fault or interface, similar effects arise leading to the well-known fringe contrast of planar defects.

4.4. Phase Contrast and HREM

If the full resolving power of a TEM is to be utilized, one has to resort to phase-contrast. In principle, all there is to do is to omit the objective aperture and to form the image by the interference of transmitted and diffracted beams. Since the diffraction pattern is the Fourier-transform of the scattering potential, a second Fourier-transformation should reconstruct the image, provided the phases of the electron waves are conserved.

HREM faces two major problems: Firstly, the final image will be two-dimensional whereas the specimen is three-dimensional - what is the relation between image and object? Secondly, a real TEM will not preserve the phases of the electron waves in the image-forming process and thus will introduce "artifacts" into the image. For ease of understanding, however, the case of an "ideal" object and an "ideal microscope" shall be discussed first.

An ideal object, e.g., would be a Si crystal only a few atom layers thick. An ideal microscope would re-transform all the spatial frequencies contained in the Fourier-transform of the object that are smaller than the resolution limit without distortions and would completely surpress all spatial frequencies above the resolution limit. The image then would consist of the projected potentials of the specimen; i.e. the charge distribution projected onto the lower specimen surface. It is obvious that the projected potentials would only form an ordered pattern if at least one set of lattice planes with a spacing larger than the resolution limit is parallel to the electron beam. Then the image could consist of bright and dark lattice fringes running parallel to the lattice planes and having the proper spacing. If a low-index direction of the specimen is parallel to the electron beam, a direct lattice image is obtained. If the resolution of the (ideal) microscope is good enough, the columns of atoms parallel to the electron beam would appear as dark dots at the proper position.

Real objects are usually thicker than just two or three atom layers. The dynamical effects discussed before then lead to intensity fluctuations of the diffracted beams and at specific thicknesses the intensity of diffracted beams may be zero so they will not contribute to the image. Fig. 9 illustrates that for the case of 110 oriented Si.

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A real microscope, finally, introduces extra phase-shifts in transmitting the electron waves. This effect is treated with the aid of the so-called contrast-transfer-function (CTF) of the objective lens which, in a way, can be considered to be a "filter" leading to an enhancement of some spatial frequencies and to a damping of others. The CTF is a sensitive function of microscope and imaging variables; especially important are the defocus-value of the objective lens, the abberration coefficients of the lens, the beam coherency, and alignment parameters as astigmatism and optical-axis control. Fig.   shows typical CTF's for different defocus values and makes clear that the image of a given object can look quite different depending on the CTF employed.

Given the difficulties encountered with real objects and real microscopes, HREM may appear to be of little value. But that would be a misconception because there are ways of interpreting HREM images without too many ambiguities and to obtain information not otherwise obtainable. With advanced computational methods now routinely applied (cf, e.g., /   /), HREM images can be simulated in great detail, taking into account all the crucial parameters of object structure and imaging conditions. A comparison of simulated and real images than may allow the interpretation of images on an atomic level. This approach is called structural imaging to distinguish it from mere lattice imaging; it demands clear and crisp micrographs taken under well-known and controlled conditions.

On a less ambitious level, lattice images still can be interpreted all the restraints and insufficiencies of "real" HREM, crystal lattice structures and crystal-lattice defects, too, are often identifiable on any lattice-image that is not too erratic. The image of stacking-faults in Si, e.g., has been simulated for practically all possible combinations of specimen thickness and imaging conditions / / and, although the images do not always look like the "direct" image of a stacking-fault, it is always possible to identify the defect.

A similar statement applies to terminating lattice fringes. There are conceivable cases where a lattice fringe may appear to terminate without a defect being present, but these situations are rare and generally easily recognized. As a rule, a terminating lattice fringe indicates the presence of a defect, usually a dislocation. The number n of lattice fringes belonging to lattice planes characterized by $\underline{g}$ which terminate at a dislocation with the Burgers vector $\underline{b}$ is given by / /

$$n = \underline{g} \cdot \underline{b} \,. \tag{3}$$

Only for n 0.7 a distinctly terminating fringe will be observed; for smaller values of n the fringes appear to be bent. Eq. (3) holds for end-on dislocations (dislocation line parallel to electron beam) and inclined dislocations. In the latter case many fringes may terminate along the projection of the dislocation line and n is determined by adding the number of ending fringes algebraically; i.e. with a plus or minus sign depending on the direction from which an ending fringe approaches the dislocation line. Eq. (3), however, does not hold for fringes terminating at interfaces; this will be discussed in detail in chapter .

A special case of phase-contrast is the Moirée contrast. Moirée contrast generally is due to interference of electron-waves from different crystals and is often observed in regions where crystals overlap. It may be observed, e.g., in HREM images of silicide layers on Si if conventional specimens are used.

5. Applications of TEM to Silicides

5.1. Conventional Samples and Standard Techniques

In this chapter a typical example of a standard TEM investigation of silicides will be given; highlighting the kind of results obtainable with minimum efforts as to specimen preparation and TEM techniques. Some of the illustrations from the investigation of Iridium-silicides reported in / / may serve this purpose; there are of course other examples, too / /.

In / /, n-type, 10 cm 100 and 111 Si-wafers were used and 20 nm of Ir was deposited at 200 °C by electron-gun evaporation in UHV. After the Ir-evaporation the wafers were annealed at 300 °C, 400 °C, 500 °C, 600 °C or 960 °C, respectively, in a He-atmosphere. 2 x 2 mm squares were then cut from the wafers and chemically thinned from the backside. A TEM investigation in a 200 kV microscope yielded the micrographs shown in Fig. from which the following results are obtained:

i) The evaluation of the diffraction patterns shows the presence of the following phases: Ir at 200 °C; Ir and a small amount of IrSi at 300 °C and 400 °C, IrSi and a small amount of Ir_2Si_3 at 500 °C and only Ir_2Si_3 at 600 °C and 960 °C.

ii) All silicide layers are polycrystalline. Because the grains are oriented at random, they diffract various intensities out of the main beam and thus appear in all shades between black and white. The grain-size is easily measured and was found to be 6 nm at 200 °C (Ir grains); 10 nm at 300 °C (Ir grains), 30 nm at 500 °C (IrSi grains) and 300 nm or 5000 nm at 600 °C or 960 °C, respectively (Ir_2Si_3 grains).

iii) All films are rather homogenous; there are no pin-holes. In the large Ir_2Si_3 grains bend-contours are observed, indicating the presence of strain in the silicide layer.

iv) The large Ir_2Si_3 grains at 960 °C would allow controlled contrast experiments and thus the imaging of defects in the silicide or interface, if so desired.

So far, no special techniques were needed with respect to specimen preparation or TEM operation and the results presented do not require more than a few hours each for specimen preparation, TEM work and the evaluation of the micrographs. There is, however, more that can be learned about Ir-silicides by using somewhat more refined techniques. Two examples shall be given; for details the reader is referred to /   /.

Two items will be discussed; i) To what extent is the IrSi observed at 300 °C covering the sample and ii) did the specimen preparation introduce any artifacts, e.g. by etching off parts of the silicide layer? Both questions can be answered by dark-field microscopy. The objective aperture now is placed over one of the IrSi diffraction rings; Fig.   shows the dark-field picture obtained. The corresponding bright-field picture and the diffraction pattern (with the position of the aperture indicated) is also shown. Only those IrSi crystals are visible that diffract electrons into the area covered by the aperture; Ir crystals and IrSi crystals diffracting into a different area are completely invisible. If the aperture would be moved to a different position on the diffraction-ring, a different set of IrSi crystals would light up. From that it is easy to estimate that IrSi crystals cover about 30 % of the total area.

In the micrographs shown so far only the Ir or Ir-silicide layer have been present, the Si substrate has been completely etched off. This leaves some doubts whether or not parts of the silicide have also been etched off. Fig.   therefore shows a micrograph that includes parts of the Si substrate (darker regions). The Si substrate displays thickness fringes in bright-field and is completely invisible in dark-field since no silicon reflection was admitted into the objective aperture. The distribution of IrSi crystals is essentially identical in areas with or without the Si substrates proving that the specimen preparation did not produce changes in the silicide layer.

The micrographs shown so far do not contain any information about the depth distribution of the various phases. The implicit assumption made in / / that the IrSi is located at the Si-Ir interface cannot be infered from the micrographs. Depth information in TEM can be obtained by stereomicroscopy; i.e. by taking two pictures under different angles of illumination. However, the contrast must not change and that, in the case of diffraction contrast, requires that both pictures have to be taken with the same g-vector and excitation error. This is possible for single-crystalline specimens if the g-vector is also the axis of rotation of the specimen between the two pictures. In the case of poly-crystals it is obviously impossible to maintain the original diffraction conditions in all grains during a specimen rotation and this excludes stereomicroscopy in poly-crystals. Depth information therefore can be obtained only with cross-sectional specimens which will be discussed in the next chapter.

5.2. Cross-Sectional Specimens

Two samples shall be discussed in some detail: The formation of Pd_2Si and PtSi on slightly oxidized substrates / / and the formation of PtSi from co-deposited Pt-Si layers / /.

In most experiments and applications concerning silicides the metal is evaporated onto a Si substrate that is covered with native oxide; 0.8-1.5 nm in thickness. It is known from numerous observations that this SiO_2 layer can influence the formation and the properties of the silicide / /. It was therefore of interest to study silicide formation on intentionally oxidized substrates. For that purpose four Si 111 wafers were cleaned with standard procedures and then boiled for 10 min. in a mixture of $NH_4OH:H_2O_2:H_2O$ (1:2:7). This procedure leaves an oxide layer of 3-4 nm in thickness. Two wafers then were etched in diluted HF to remove the oxide and all four wafers were quickly inserted into the evaporation apparatus. 50 nm of Pd and Pt was evaporated onto a "clean" and "oxidized" wafer, respectively. All wafers were then annealed at 400 °C for 1 hr in the atmosphere.

14 After the annealing, cross-sectional as well as conventional specimens were prepared from all four wafers. Fig. 14 shows typical micrographs obtained from the Pd-evaporated cross-sectional samples. On the clean substrate, a rather nice and well-developed Pd_2Si layer has been formed (Fig. 14a). That it is Pd_2Si is easily verified from the diffraction pattern. The interface is straight and sharp and only occasionly slightly disturbed by a potruding grain of Pd_2Si. The diffraction pattern shown in Fig. 14a shows that the Pd_2Si layer is epitaxial to the Si substrate. This diffraction pattern also demonstrates a major short-coming of cross-sectional specimens: high-quality diffraction patterns are not easily obtained. This is so because the diffraction pattern originates mostly from the Si substrate, with only little intensity from the silicide layer, and additional erratic spots from the support-Si glued to the cross-section investigated (usually another specimen) as well as "amorphous" rings from the epoxy. Only if the silicide layer is epitaxial and the specimen is tilted to a low-index orientiation an interpretable diffraction pattern will be obtained. If the silicide layer is polycrystalline, at most a few grains will contribute to the diffraction pattern and produce only a few diffraction spots that give hardly sufficient information for phase identification. Therefore it is always advantageous to investigate conventional specimens parallel to the cross-sectional samples.

Going back to Fig. 14 one notices that the Pd_2Si surface is considerably rougher than the Si-Pd_2Si interface. The micrographs show no details that may be caused by artifacts and it is quite certain that the cross-section gives a true and representative picture of the Pd_2Si layer formed on a clean Si wafer.

The micrographs from the oxidized substrate (Fig. 14b) are distinctly different from those of the clean substrate. To be sure, a Pd_2Si layer was formed again (as verified by diffraction patterns from conventional specimens), but in a much more haphazard way. The interface is wavy, quite irregular and always shows some diffraction-contrast effects; indicating strain-fields; the silicide surface is exceedingly rough. The most distinctive feature is the "band" of irregularly shaped bright contrast features which is located in the lower half of the silicide. Since the contrast is mostly mass-contrast, these bright contrasts are either due to voids or to inclusions with a lower scattering factor than Pd_2Si. The most plausible assumption is that these features are remnants of the oxide layer. This assumption is corroborated by Auger depth-profiling experiments performed with specimens from the same wafer / /. A more direct proof could come from STEM in the analytical mode where a chemical analysis of the inclusions should be possible using the microprobe or electron-energy-loss spectroscopy facilities.

If the bright contrast features are oxide remnants, one would expect to observe similar features, albeit smaller, in the Pd_2Si layer formed on the "clean" substrate because that substrate, too, was covered with the unavoidable native oxide layer. The oxide remnants to be expected would be in the 1-2 nm region, which is just about the resolution limit for voids or inclusions, and therefore might be overlooked quite easily. A systematic search among old micrographs of Pd_2Si layers on "clean" substrates revealed several micrographs where a barely visible band of small bright dots at about the expected depth position was
16 observed; Fig. 16 gives an example. This picture also demonstrates the limits of mass-contrast TEM; the micrograph shown in Fig. 16 is about the optimum one can hope to achieve with the particular TEM used in this case. An additional problem often encountered with micrographs like the one shown in Fig. 16 is that the details of interest, although perfectly visible in the negative, are easily lost in the final print in a journal or book; no matter how carefully printing was done.

The band of oxide remnants has been found in Pd_2Si layers formed on 100 and 111 substrates under various conditions. It thus appears to be a typical feature of Pd_2Si formation and may be used to deduce some details of the Pd_2Si formation process as, e.g., the relative magnitude of the diffusional fluxes of Pd- and Si-atoms /   /.

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The same kind of investigation as described above was also performed in the Pt case; typical micrographs are shown in Fig. 16 . On the clean substrate PtSi was formed (as ascertained from the diffraction pattern of conventional specimens). Although the PtSi-layers in Fig. 16 are too thick for TEM (a rather common occurence with cross-sectional specimens), it still can be seen that the Si-PtSi interface is rather rough and the PtSi surface relatively smooth. On the oxidized wafer the situation is more complex. Layers of unreacted Pt alternate with irregularly shaped lumps of PtSi (the phases again identified by diffraction pattern from conventional specimens). At higher magnifications (Fig. the thin oxide layer between the Si substrate and the Pt is visible as well as structural details within the PtSi. A search for oxide remnants in the PtSi on the clean substrate failed because the PtSi layer was too thick to allow the detection of small particles.

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It is worthwhile to compare micrographs from conventional samples to those from cross-sectional samples. Fig. 17 shows the Pd_2Si layer on the clean and oxidized substrate and it can be seen that they do not appear all too different. Both show some structural defects; mainly anti-phase boundaries and small-angle grain boundaries, and both are epitaxial to the substrate as indicated by their diffraction patterns. Most noteworthy is that there are no traces of the oxide remnants observed in cross-section.

The examples given clearly demonstrate that cross-sectional samples may yield information practically not obtainable from conventional specimens. They also demonstrate the weaknesses of the technique with respect to phase identification by diffraction techniques.

One more example of cross-sectional TEM shall be given: PtSi formed from co-evaporated Pt-Si layers. If some Si is added to the evaporated metal, the silicide forms partially by reacting with the Si present in the evaporated layer and thus consumes less Si from the substrate, reducing the penetration depth. Experiments were undertaken with various mixtures of Pt and Si; full details 18 can be found in / /. Fig. 18 shows a cross-sectional view of the PtSi layer formed after evaporating $Pt_{67}Si_{33}$. Only about nm of the total PtSi layer would be expected to form by reaction with the substrate. The outstanding feature of Fig. 18 is the string of white dots visible in the PtSi layer and located at a distance of nm from the Si-PtSi interface. This band of bright dots has also been observed for other compositions of the evaporated Pt/Si layer; its position in the PtSi always corresponds to the upper half or even top-surface of that part of the PtSi layer that is formed by reaction with the substrate. In analogy to the Pd_2Si-case, the bright dots are interpreted as remnants of the native oxide layer.

In this case it was tried to detect the inclusions of oxide in conventional specimens, too. Very thin specimens are needed for such an undertaking therefore most of the PtSi layer was removed by ion-milling and chemical etching from the backside produced the final specimens. A careful TEM search for small inclusions using the approbriate techniques (mass-contrast; defocus-series) finally yielded some contrast features that could be interpreted as the oxide remnants; the micrographs, however, were not convincing. It appears fair to say that the oxide remnants would never have been detected with conventional TEM.

The examples presented convincingly demonstrate the power of XTEM. The dramatic influence of the oxide-layer on a Si-substrate on the formation of silicides is obvious, particularly in the Pt-case. But the Pd-case, too, shows a remarkable sensitivity to substrate surface-conditions and it should be emphasized that methods other than TEM (e.g. glancing-angle x-ray cameras, Rutherford back-scattering) would not have shown significant differences between the Pd_2Si layers on the clean and oxidized the Pd_2Si on the clean wafer. It might be speculated that a stress-induced or stress-enhanced corrossion process can take place in an atmosphere containing traces of HF and that the layer of oxide remnants can act as the rapidly decomposing interfacial layer required in such a process. This effect may also be the reason why Pd_2Si layers on cross-sectional specimens tend to peel-off: the large interface-area exposed to a potentially corrossive atmosphere may facilitate this process.

The oxide particles may also be regarded as "markers" (cf. / /), pinpointing the relative magnitude of the diffusive fluxes of Si and the metal. If only the metal (or Si) would be the diffusing species, the oxide particles would end up on top of the silicide layer (or at the interface, respectively). The co-evaporation study of the Pt/Si system gave indirect evidence for the oxide being on top of the PtSi, whereas in the Pd_2Si case it was well within the silicide. This indicates that during the formation of PtSi only Pt is diffusing; while both Pd and Si atoms diffuse during the formation of Pd_2Si. This conclusion is corroborated by tracer measurements / / and marker experiments with Ar bubbles as markers / / and raises the question why the microscopic mechanisms of PtSi or Pd_2Si formation are so obviously different.

The deduction of diffusion mechanisms from oxide-particle position is only correct if the oxide particles are completely inert, i.e. do not migrate and do not influence the reaction / /. These conditions certainly are not always fully met by oxide markers, but it appears likely that specimens with defined oxide layers having geometries particularly suited to XTEM (e.g. thin stripes of oxide, 3-4 nm in thickness, alternating with "clean" areas) would provide considerable insight into the microscopic formation mechanisms of many silicides.