Summary

Nickel silicides are widely used in making electrical contact to complementary metal-oxide-semiconductor (CMOS) devices in advanced integrated circuits. They have been the preferred contacting material since the 2006 “65 nm technology node”, partly because a self-aligned-silicide (“SALICIDE” [1]) process is available. However, their high temperature behaviour is complex and, crucially, improved by the presence of platinum.

Seminal information [2] on the influence of the Pt in limiting the formation of the undesirable NiSi2 phase during annealing was obtained kinetically using real-time RBS [3] (see Figure), where the very large quantity of data resulting is analysed in real-time by an artificial neural network (Barradas & Vieira, Phys. Rev. E, 2000 [4]).

This is an important example, but only one of many quantitative operando RBS [5] observations of diffusion and phase separation during annealing of multilayer samples. Operando measurements can be extraordinarily efficient compared to a conventional “cook and look” approach, and indeed readily give details of processes that are hard (or impossible) to obtain conventionally.
Clearly, Rutherford backscattering spectrometry (RBS) is ideal for observing silicidation processes, since the metal signal is background-free and the depth resolution is well matched to the application. Figure 2 shows conventional RBS of the important Ni:Pt system (Corni et al, Appl.Surf.Sci., 1993 [6]).

**Figure 2:** Silicidation by “cook and look”

100 nm Ni (5%Pt) on Si with 30 min isochronal annealing at various temperatures, observed by 2 MeV He-RBS. For the annealed samples and the Pt signal, the arrow indicates the position of the interface.

Figure 3 of Corni et al, Appl.Surf.Sci., 1993

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**Figure 3:** Silicide formation during annealing observed in operando

2 minute spectrum obtained at 375 °C (see line on Figure 1).

Figure 3 of Demeulemeester et al (Appl.Phys.Lett. 2008)
The Ni:Pt/Si system is very complex however, and the presence of Pt has intricate effects on the interplay between the two phases, Ni$_2$Si and NiSi. This is most clear from the operando observation of the complete silicidation process (Figure 1), a single spectrum from which is shown in Figure 3 where the segregation of Pt out of the di-nickel silicide and the onset of the formation of the monosilicide can be seen.

**Figure 4**: RBS analysis in operando of the Ni:Pt/Si system
75 nm Ni/Si alloyed with (1, 3, 7, 10) at% Pt and annealed at 2°C/min
Figure 1 of Demeulemeester et al (J.Appl.Phys. 2013)

**Figure 5**: Activation energy data by in operando RBS
For each sample composition, raw data were obtained in one single anneal run (see Fig.4). Film thicknesses were extracted from the raw spectra by ANNs and fitted (red lines) to obtain activation energies
Figure 6 of Demeulemeester et al (J.Appl.Phys. 2013)

Further work by Demeulemeester et al (J.Appl.Phys. 2013) [7] on this important system has shown the sensitivity to the Pt content (see Figure 4). They successfully applied real-time RBS in combination with artificial neural network analysis to disentangle the growth kinetics during the complex growth of Ni(Pt) silicides and showed that activation energies can be extracted from a single ramped real-time RBS measurement (see Figure 5).
Complementary work on the same system included real-time X-ray diffraction (XRD: Demeulemeester et al, J.Appl.Phys. 2013 [8]) and atom probe tomography (APT: Mangelinck et al, Scripta Materialia, 2010 [2]). RBS allows the phase formation and the redistribution to be followed in situ and thus gives crucial information of the different steps of the redistribution. But RBS has relatively poor depth resolution and, for these nanocrystalline materials, effective no lateral resolution. APT is an ex situ but very high resolution tomographic method giving highly detailed structural information (see Figure 6). Operando RBS gives a broad overview of the entire process, where APT follows inhomogeneities at the nano-crystalline level. This is similar to the complementarity between RBS and transmission electron microscopy (TEM).

**Figure 6: Nano-structure of 300°C annealed Ni:Pt/Si by APT**

50 nm Ni (5%Pt) on Si annealed at 300°C for 1 hour with in situ XRD. Image is 120x400 nm

**Left (120 nm thick slices):** (a) APT image of Si & Ni distribution; (b) APT image of Pt distribution; (c) reconstruction of structure.

**Right (thin slices):** (a) top view of 20 nm slice in NiSi phase shows Pt enrichment at grain boundaries; (b) top view of 20 nm slice in NiSi phase shows that this phase is discontinuous; (c) slice as for (b): high levels of Pt are present at grain boundaries

Figures 1 & 2 of Mangelinck et al (Scripta Materialia, 2010)


What is different here is the use of artificial neural networks (ANNs) to handle the huge datasets produced quantitatively. The critical thing for an ANN is how to “train” it. A “training set” must be constructed to allow the network to assign the proper weights to all its nodes so that the inputs elicit the correct outputs. There are three essential things to understand about ANNs: (i) the ANN can only interpolate within its training set, it cannot extrapolate out of it; (ii) the ANN knows no physics! and (iii) the response of the ANN is effectively instantaneous. This is all described in detail by Barradas & Vieira, (Phys. Rev. E, 2000) [4].
ANNs have had some bad press because it is easy to train them badly: they will always give an answer, but the answer can be complete nonsense! However, in the cases we have described the answer has been demonstrated to be reliable. Figure 7 shows the systematic way this is done for real-time RBS.

The ANN used by Demeulemeester et al, (NIMB 2010) [5] is trained with a complex training set of 18000 spectra and a test set of 2000 spectra (generated automatically by the DataFurnace [12] code). But all 63 spectra shown in Figure 7 are analysed for the thickness of the various phases (with appropriate “roughness”) by the trained ANN in a fraction of a second. The ANN output is then fed into DataFurnace as an initial “guess” at the structure implied by the spectrum, and fitted using a proper physical model [13] (which is known very well!). Clearly, Figure 7 shows that the ANN was very well trained! Equally clearly, the inversion of the RBS spectra (mathematically an ill-posed problem [14]) can now be done entirely automatically! It is a huge advance to be able to fit very large numbers of RBS spectra – and fit them effectively perfectly, thus extracting approximately all their information – without any intervention by the analyst. This procedure works even for very complicated RBS spectra, that have traditionally been a nightmare for the analyst. The analytical difficulty is now transposed to constructing the proper training and test sets for the ANN.

There is even a suggestion that RBS without humans [15] is possible, proposed by Barradas et al (Phys.Rev.E, 2002) [16]. They demonstrate that it is possible to create an algorithm based on ANNs, “which is able, for a given system [in their case Ge-implanted Si], to optimize the experimental conditions for each sample and then analyze the final spectrum collected. The algorithm is easily extensible to other systems. Once this algorithm is implemented in a code connected to an experimental setup with automated sample loading, this will lead to the performance of RBS experiments entirely without the assistance of humans.” Importantly, Barradas et al here demonstrate that ANNs can successfully be developed that are able to warn if a spectrum falls outside the training set: this would be an essential safeguard for any automatic system.
However one views “RBS without humans”, what is certainly true is that IBA methods currently depend very heavily on the expertise of the analysts. IBA is expensive! But there are surely “routine” cases which ought to be amenable to automation, so that the price per analysed spectrum is reduced? This works says that indeed there are, and moreover that we know how to treat them!

On a separate issue, this work is limited as it stands to annealing only to about 600°C, because hotter samples will necessarily generate higher energy photons, and the semiconductor detectors are light-sensitive. But we should note that there is a completely different detector technology impervious to sample temperature. Muller et al (NIMB, 2011) [17] has described a very simple gas ionisation detector with a performance comparable to the semiconductor detectors for He-RBS. These devices have greatly enhanced energy resolution for ions heavier than He, operate equally well in the light or at high temperatures, do not suffer from beam damage, and can support very high count rates. They could transform this application, and IBA in general.

Keywords

Real-time, Artificial Neural Network, ANN, silicide, SALICIDE, CMOS, annealing, operando, automatic analysis, gas ionisation detector

Thin Film Modification Methods

Sputtering, ion implantation

Complementary Analytical Methods

RBS, XRD, APT (atom probe tomography)

Cited Literature


