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PHASE GROWTH ANALYSIS IN METAL SILICIDES

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Abstract

In this paper we show how different techniques and their combination can be used to follow the phase formation in a-Si/Cu and in the a-Si/Ni system, moreover under which conditions these techniques can be useful and what kind of information they can provide.

We show how a combination of experimental methods of GIXRF (grazing incidence x-ray fluorescence) analysis and x-ray standing waves (XSW) technique can be used for the non-destructive depth profiling of a-Si/Ni/a-Si layers with nanometer resolution to monitor the phase growth. Moreover we demonstrate how the combination of SNMS, (Secondary Neutral Mass Spectrometry), profilometer, XRD and APT (atom probe tomography) can be used to follow the initial state of phase growth between the amorphous Si and nanocrystalline Cu thin films.

I. Introduction

Metal silicides are well known and wildly applied materials in numerous different scientific fields from computer technology to power sources for their manifold and favorable properties and bridge position in our silicon based technological world.

1) The properties of nickel silicide thin films have taken on importance for advanced technologies in state-of-the-art microelectronic devices [1-8] because of its favorable properties as contact material. The phase sequence and

identification has been discussed in the past [6,1]. Depending on the Ni film thickness, the Ni_2Si, Ni_3Si_2 and $Ni_{31}Si_{12}$ phases had been observed and the initial phase to form was a strained Ni_2Si layer [6,1]. This strain in the silicide layer remains until the Ni film is completely consumed.

2) Thin, crystalline silicon (c-Si) films are key materials for low cost high efficiency solar cells [1,2] as the maximum efficiency of amorphous silicon (a-Si) solar cells is still restricted by the structural metastability and disorder of the films. However, physical vapor deposited thin Si films are usually amorphous and the crystallization temperature of Si is very high (~1000 K) which requires expensive, heat resistant substrates (for example quartz glass) and high thermal budgets. The maximum possible temperature for different substrates can be seen e.g. in Fig 1 of [1]. Metal induced crystallization (MIC) offers a different ways to circumvent this problem as the crystallization temperature of Si in contact with certain metals is drastically reduced (see [13]). In case of silicide forming materials such as Ni [1] the silicide acts as a template for nucleating c-Si. Cu is well known to form multiple silicide phases [1] and previous investigations had shown that MIC process proceeds with the aid of Cu_3Si phase [1,2]. In some cases the Cu and the Si is used to create the new generation of optical data storage Blue-ray discs. Meanwhile in the field of power sources especially in Li-ion secondary batteries, the traditional graphite anodes have been replaced by Si nanowires or nanorods that possess higher specific capacity and enlarged surface areas. The increased energy density and faster charging-discharging process however coupled with some unpleasant drawbacks [1]. Because of the structure and the anode's large volume change during the insertion and extraction of lithium ion the battery structure loses its initial shape and electric properties quickly, which shortens the lifetime of the battery. Previous investigations [1,2] showed that these problems could be overcome by co-deposition of Cu and Si or by a Cu coverage of the structure. In these cases the presence of the Cu_3Si phase was proved by XPS and XRD measurements and the improvement of the electric and structural properties afterward were reported. Her et al. observed the appearance of this phase between 370 and 520 K [17]. Moreover, Ou et al. reported the formation of crystalline Cu_3Si grains in the as-prepared layer [1]. The kinetics of the phase growth in the 450-500 K range was found to be parabolic by Chromik et al [1], whereas in some Metal/Si systems non-Fickian phase growth kinetics was observed (see e.g. [1]).

Earlier in [1], our department demonstrated a method for measuring the nanoscale shift of interfaces in the same Ni/amorphous-Si system and a similar experiment to this was performed in a-Si/Co system [1]. It was shown that the reflection on the interface between media with different refraction indices is used to produce XSW. The phase difference between the incoming and the reflected beam depends only on the distance from the sample surface or layer thickness. As a considerable interaction between the beam and the matter on the substrate (i.e. the sample to be measured) can take place only in the region of high electric field power, and it can be used to gain depth selective information form the sample. Amplification of the fluorescence intensity pattern can be achieved by putting the sample in the space between two reflecting layers [25]. If the refraction index of the reflector layer is significantly larger than that of the spacer material, the beam is going to be bounced back and forth from the walls several times before being absorbed. The multiply reflected beam is going to interfere with itself, and at certain incident beam angles the electric field may form standing wave-like patterns

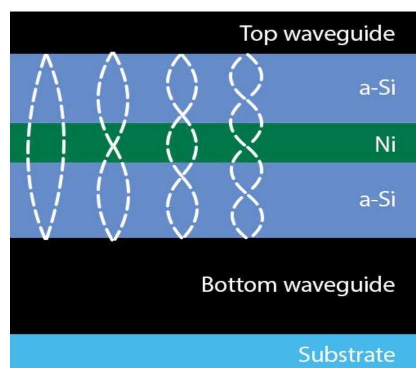

Figure 1: The schematic figure of the deposited layer structure and the formed XSWs within. [25]

On the other hand numerous articles and publications can be found with detailed description of another depth profiling technique, called SNMS (Secondary Neutral Mass Spectrometry) [1-5]. In this case the depth profile of a given sample is obtained by the removal of the the atoms located on the

surface due to the impact of ion bombardment. This technique as compared to the previously described x-ray based technique however requires a number of samples for a detailed experiment due to its destructive nature.

In this paper we report our results obtained from the experiments performed at a synchrotron light source facility [1], achieved by the software developed by a member of our department and measurements based on SNMS and profilometer measurements in order to determine the composition profile and the latter phase growing in a-Si/Ni/a-Si samples and in a-Si/Cu samples. The results of the latter one have been supported by APT measurements performed by our colleagues at the University of Münster.

II. Experiments & Results

The sample were prepared for both experiments in a custom built magnetron sputtering system at high vacuum conditions (base pressure = ~ 10^{-7}mbar), and with a dynamic flow of high quality Ar gas at a pressure of ~ 10^{-3} mbar during the deposition. For the XSW measurements samples with Ta(5 nm)/a-Si(12 nm)/Ni(10 nm)/a-Si(14 nm)/Ta(30 nm)/SiO_2(substrate) structure while for the SNMS measurements samples with Cu(45 nm)/a-Si(120 nm)/SiO_2(substrate) structure had been prepared.

1) For the XSW measurements a simultaneous reflectometry and GIXRF measurement were performed to measure the composition profile of the multilayer sample. PIN photodiode detector was used for measurements of reflected (diffracted) beam. An energy dispersive detector was used to record the fluorescence spectrum of the sample.

We used the simple approach of Parratt. [1-3] Therefore, if the sample structure is known, it is possible to calculate the electric field generated by the incident beam, and so theoretically we can calculate the fluorescence intensity according to the following formula

$$I(\theta) = \int_0^L c(x) E^2(\theta, x) dx \tag{1}$$

where c is the atomic fraction of the material in interests (Ni), E is the amplitude of the electric field, L is the length of the sample – waveguide layers included, and is the incident angle. Changing the incident angle, the electric field also changes, i.e. the positions of nodes and anti-nodes (see Fig1).

On the basis of the previous equation, it is possible to determine the fluorescence radiation intensity versus the angle of incidence.

Since the fluorescence intensity can be measured and calculated the development of the structure i.e. the change in the layer structure due to the heat treatment (at 503 K) performed at high vacuum conditions can be extracted and plotted. So thus we can follow the variations of our sample in a non-destructive way.

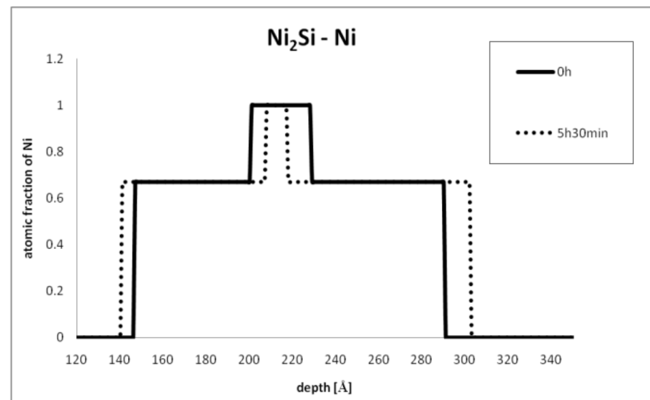

Figure 2: Reconstructed layer structure of an annealed (5.5h – dotted line) and the as-deposited sample. [1]

It can be seen that even in the as-deposited sample a mixed region of Ni and Si appeared corresponding to a composition of ~67% Ni and ~33% Si from which mixture the Ni_2Si phase formed and kept on growing later. This techniques does not simply give us the structure of the sample and make it possible the follow the phase growth within but as in Figure 2 can be seen it pinpoint the existence of such a mixed layer at the interface of as-deposited samples as well. However for samples prepared by magnetron sputtering technique such a mixed layer is not unique.

2) The measurements performed on the Cu/Si samples separated in two main steps. At first we bored the sample with the SNMS in real time mode and which one was followed by measuring the bored crater with a profilometer (AMBIOS XP-1). In order to identify the position of the growing phase we followed not only the masses of the Cu and the Si but the CuSi molecule as well. Since this molecule formed either in the plasma of the SNMS or ejected from the surface is a good marker of that both material was present in the same time. Setting the half intensity position of the CuSi signal as the interface position of the growing Cu_3Si phase thanks to the real time mode of the SNMS we are able to stop the bombardment at the two interface position of the phase in interest and can measure by the profilometer their depth. Previously determining the initial position of the Cu/a-Si interface setting it as a 0 position the latter change in the structure can be plotted.

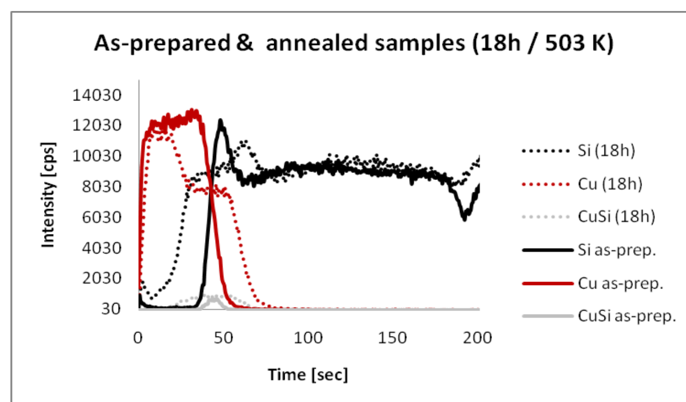

Figure 3: The SNMS profiles of an as-prepared and an annealed (18 hours at 503K) samples.

We performed heat treatments and the combination of SNMS and profilometer measurements for different times in order to gain a detailed image about the initial state of phase formation in Cu/a-Si system.

In order to identify the phase forming during the heat treatments XRD measurements were also done. The XRD measurement proved the appearance of the Cu_3Si phase in the annealed sample.

However, it is possible to reconstruct the depth profile from the raw SNMS profiles, this time for the sake of simplicity we plot the the raw SNMS profiles only, since at this point there is no need for such a depth profile for determining the thickness of the growing phase. Here we preferred to use the profilometer measurements for this reason.

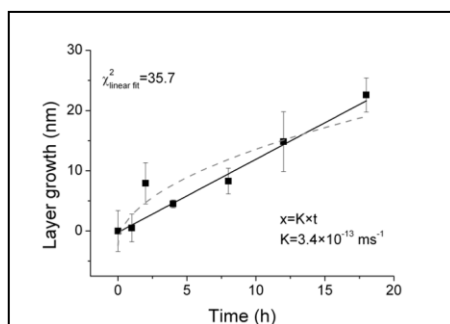

Figure 4: the layer growth of Cu_3Si versus annealing time (in hours), fitted in linear and parabolic way (dashed line) [1].

From the obtained data we concluded linear growth kinetics for the Cu_3Si phase at 503K.

Interestingly the two interfaces showed similar shift during the time of the annealing. In spite of the stoichiometry of the Cu_3Si phase that would have suggested larger Cu consumption, we found a slightly larger Si consumption instead. The above results could come, according to our understanding, from the grainboundary diffusion of Si in the polycrystalline Cu, which could shrink the size of the Si layer and at the same by increasing the Si content of the Cu layer enlarging its size as well.

This hypothesis was supported by APT measurements later (see below). Clear evidences of grainboundary diffusion of Si were found, thanks to the 3D, atomic resolution pictures gained by this technique. [**Hiba! A könyvjelző nem létezik.**]

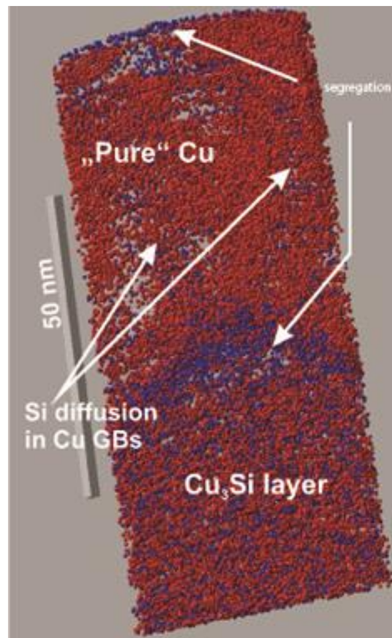

Figure 5: a section from an APT measurement of an annealed specimen, red balls are Cu and blue balls are Si atoms. The surface and interface segregation of Si as well as the grain boundary diffusion is clearly visible. [36]

III. Conclusions

As we could see in the case of these separate techniques represented here, the measurements concerning the phase growth of metal silicides can be followed in various ways. Depending on the circumstances: such as the amount of available samples, or reachable technology or the desired information about the structure or its change these techniques present a useful and prosperous way

of analytical work and highlight the importance and usefulness of the combination of different techniques.

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