ACTA PHYSICA DEBRECINA XLVII, 175 (2013)

INVESTIGATION OF SOLID STATE REACTIONS BETWEEN Ni_2Si NANOCRYSTALLINE FILM AND Si SUBSTRATE

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Abstract

The subject of my PhD work is the investigation of diffusion and solid state reactions in Ni/Si system. As first step I investigated the Ni_2Si/Si system. Nanocrystalline-Ni_2Si/single-crystalline-Si substrate samples were prepared using DC magnetron sputtering. In my preliminary measurements heat treatments at different temperatures led to NiSi reaction layer formation. The concentration-sputtering time profiles were determined by means of Secondary Neutral Mass Spectrometry (SNMS). This new phase grows by grain boundary diffusion induced solid state reaction (GBDIREAC); i.e. by formation of this phase at the grain boundary and by growing perpendicular to the grain boundary plane.

I. Introduction

Silicides are used as contact materials and play an important role in the ultra-large-scale integrated circuit technology (ULSI) and for producing shallow junctions and Complementary Metal–Oxide–Semiconductor (CMOS) technologies. NiSi is more favorable than other silicides due to the lower consumption of Si during the silicidation process, low resistivity, low formation temperature and no resistivity increase on narrow line. [1-8].

NiSi has been largely used since the beginning of 65 nm technology node and is currently used for 45 nm node and below [9].The contacts based on NiSi are obtained by solid state reaction between metal and silicon using the self aligned silicide (SALICIDE) process [10,11]. In current process, the silicidation is performed in two annealing steps: first Ni_2Si or Ni-rich phases are formed during a heat treatment by rapid thermal annealing (RTA1), and a selective etching is used to remove the unreacted metal. Second, the low resistivity NiSi phase is obtained after a further heat treatment (RTA2). NiSi can also be transformed in $NiSi_2$ at high temperature, which is a major disadvantage for its integration in devices since $NiSi_2$ has a relatively high resistivity [12]. Another technology to produce ultrathin NiSi layer on Si; a) sputtering deposition of metal film on a Si (100) substrate, b) selective wet etch to remove the deposited metal film and leave an intermixed layer at the Si surface, and c) silicide formation induced by annealing in a rapid thermal processing (RTP) chamber at 500 °C for 5 s [13]. In these technologies in the main physical processes the key role is played by a mixed contribution of bulk and grain diffusion processes to the formation and growth of the reaction layers.

In two recent papers from our Department it has been shown [14,15] that in nanocrystalline thin films the formation of a fully homogeneous reaction layer is possible by grain-boundary diffusion only. This is the so-called grain boundary diffusion induced solid state reaction (GBDIREAC); during which the formation of these phases takes place at the grain boundaries and grows perpendicular to the grain boundary plane.

Grain boundary (GB) diffusion plays a key role in many processes occurring in engineering materials at elevated temperatures, such as Coble creep, sintering, diffusion-induced GB migration (DIGM), different discontinuousreactions, recrystallization and grain growth [16,17]. Also, GB diffusion is a phenomenon of great fundamental interest. Atomic migration in a GB should be treated as a correlated walk of atoms in a periodic quasi-2D system with multiple jump frequencies [17-19].

As it was mentioned above the formation of the reaction layer around the GBs takes place by interface process: the GBs move perpendicular to the initial GB leaving behind the reaction layer. This is similar to a diffusion induced re-crystallization, DIR, process, when the GB sweeps and leaves behind an alloyed region and can be called as grain boundary diffusion induced solid state reaction (GBDIREAC). As a result of this above process, finally even a fully reacted compound layer can be formed from the initial bilayered structure by GB/interface diffusion alone. This way of the reaction layer formation is different from the usual solid state reactions observed at higher temperatures where a compact reaction layer forms and grows parallel with the initial interface (with contributions from bulk diffusion as well) [14,15].

In our study we use the Secondary Neutral Mass Spectrometry, (SNMS) which is modern method to map concentration profiles formed and to study the solid state reactions between Ni or Ni_2Si and the Si substrate. First we investigate the solid state reaction between nanocaytalline Ni_2Si and Si substrate at low temperatures and hope to achieve the formation of a homogeneous NiSi layer.

II. Experimental Techniques

W(10nm)/Ni_2Si(20nm) films were deposited onto Si substrate by DC magnetron sputtering at room temperature. Disk-shaped Ni_2Si and W targets with diameter of 2 inches were used as sputtering sources. The thin W layer was used as a cap layer to prevent the oxidation. After etching the Silicon substrate by HF acid, the films were deposited by sputtering in Ar (99.999%) pressure of $5x10^{-1}$ Pa (under dynamic flow) and the sputtering power was 40 W. The sputtering rates were calculated from the layer thickness measured by AMBIOS XP-1 profilometer. The samples were annealed undervacuum ($1x10^{-4}$ Pa) at different temperatures.

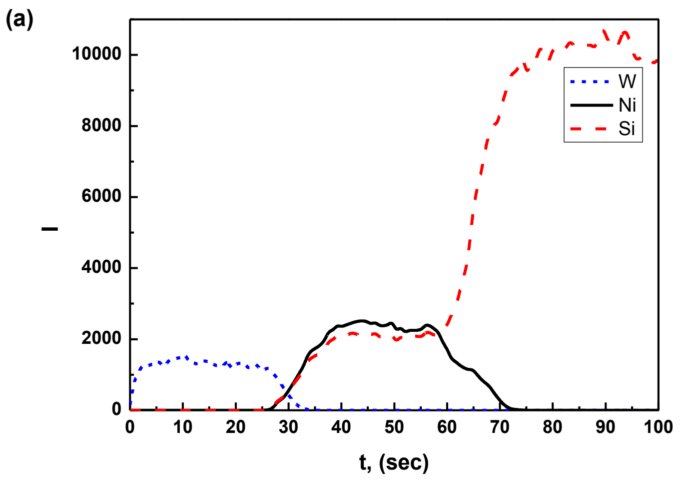
The average concentration-sputtering time profiles were measured using a Secondary Neutral Mass Spectrometry (INA-X, SPECS GmbH, Berlin). The SNMS data (intensity(cps) - time (s) spectra) were transformed to concentration - time profiles, using the sensitivity factors of the elements.

The SNMS device works with noble gas plasma and the bombarding ion current has an extremely high lateral homogeneity. The low bombarding energies (in order of 10^2 eV) and the homogeneous plasma profile result in an outstanding depth resolution (<2 nm) [15,20]. In this case, the detection limit of the SNMS is about

10 ppm. Details of quantification procedure of SNMS spectra are described in [15,21,22].

III. Result and discussion

As a first step in my studies I had to find the most appropriate time and temperature where the process will lead to the formation of homogeneous NiSi layer. Fig.1.(a) shows the intensity versus sputtering time of the as-deposited W(10nm)/Ni_2Si(nm)/Si. The W film is used to avoid oxidation of the sample during annealing. Then, the intensity was converted to concentration using the sensitivity factors of the elements as shown in Fig.1.(b). It is clear that the as-deposited Ni_2Si film is homogeneous.


(a)
I
0
2000
4000
6000
8000
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t, (sec)
0
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20
30
40
50
60
70
80
90
100
W
Ni
Si

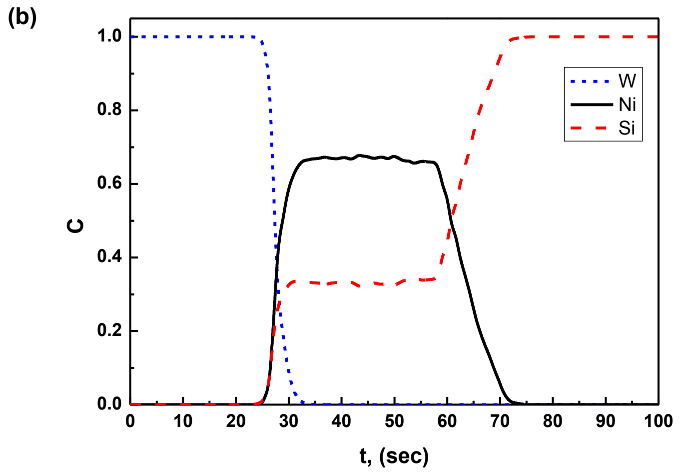
(b)
C
0.0
0.2
0.4
0.6
0.8
1.0
t, (sec)
0
10
20
30
40
50
60
70
80
90
100
W
Ni
Si

Figure 1: (a) Intensity versus sputtering time, (b) concentration versus sputtering time of the as-deposited W(10nm)/Ni_2Si(nm)/Si.

The calculated concentration-sputtering time of the sample annealed at 180 ^oC for 1 hour is shown in Fig. 2. It is seen that Si atoms diffused along the whole Ni_2Si film. But the film is still Ni rich. With increasing the annealing temperature to 190 ^oC for the same annealing time (1 hour), we observe homogeneous NiSi film as shown in Fig.3. It is obvious that there is no reacted layer at the interface. This confirms the formation of NiSi by grain boundary diffusion induced solid state reaction (GBDIREAC). This happens by formation of this phase at the grain boundary and by growing perpendicular to the grain boundary plane as shown in Fig.4.

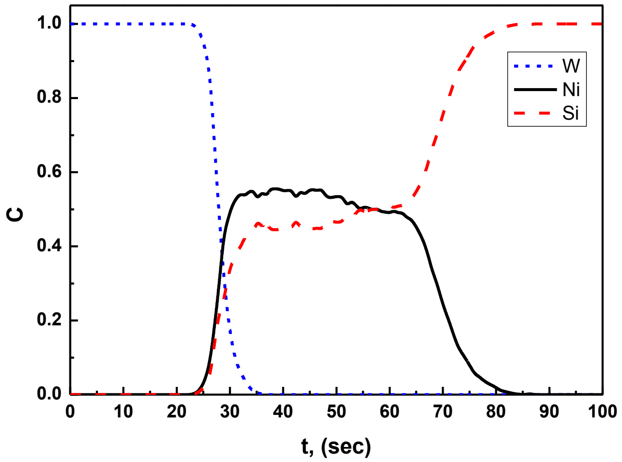

Figure 2: Concentration versus sputtering time of W(10nm)/Ni_2Si(nm)/Si annealed at 180 ^oC for 1 hour.

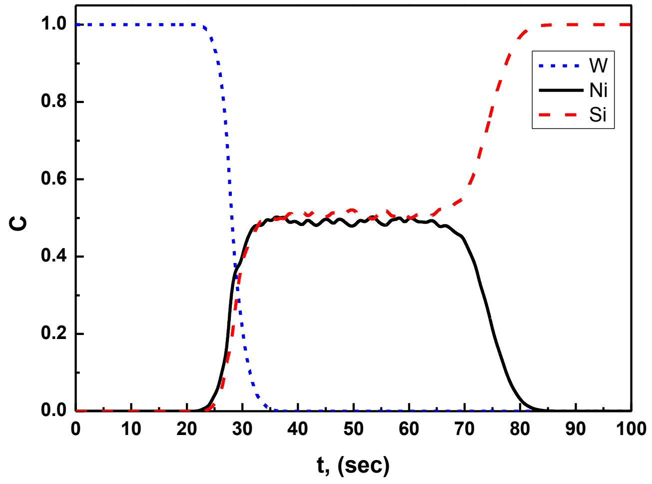

Figure 3: Concentration versus sputtering time of W(10nm)/Ni_2Si(nm)/Si annealed at 190 ^oC for 1 hour.

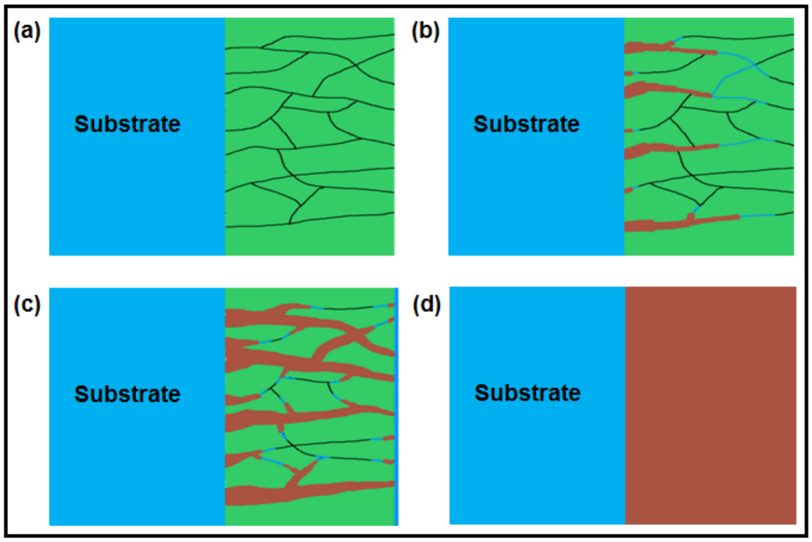

Figure 4: Sketch of grain boundary diffusion of Si (blue) into Ni_2Si film (red) forming NiSi (brown).

IV. Conclusion

Our preliminary data illustrate that grain boundary diffusion induced solid state reaction between Ni_2Si and c-Si substrate can lead to NiSi reaction layer formation depending on the temperature and time of annealing. Our future work is to study the effect of temperature, time of annealing and film thickness reaching to a certain temperature-time-thickness window inside of which the formation of NiSi is expected. Furthermore, the characterization of the film structure by XRD, TEM, electrical resistivity and DSC techniques will also be carried out.

Acknowledgments

The work is supported by the OTKA Grant No. CK80126 as well as by the TÁMOP-4.2.2/B-10/1-2010-0024 and TÁMOP-4.2.2.A-11/1/KONV-2012-0036 projects, co-financed by the European Union and the European Social Fund.

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