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A STUDY OF THERMALLY FORMED REACTION PRODUCTS IN A Ni/Cr/Si MULTILAYER STRUCTURE

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Key words: semiconductors, microelectronics, thin films, multilayer structures, diffusion, nickel silicides, differential scanning calorimeter, Auger electron spectroscopy, transmission electron microscopy

Abstract: The preparation of well characterized multilayer structures by controlling the interfacial reactions and diffusion processes is a key to a device fabrication in modern microelectronics. Silicides find widespread applications and interest since they have the appropriate electrical characteristics and together with diffussion barriers formed relatively high thermodinamic stable systems. In this work, a model multilayer structure composed of Ni, Cr and Si thin films was sputter deposited onto smooth silicon (111) substrates, having the individual film thicknesses between 20 and 60 nm in order to study the reaction products formed by thermal treatment in a differential scanning calorimeter (DSC). After the deposition one sample was examined by AES depth profiling before heat treatment, in order to control the original interfaces. The other samples were depth profiled after heating at rate of 40°C/min from room temperature to 380°C and 550°C, respectively. The AES depth profiles and TEM investigations of the samples before and after DSC measurements showed a strong reaction between the Si and Ni layers and a much less pronounced reaction between Cr and Si. The two types of Ni-silicides, i.e. Ni_2Si and NiSi, were clearly recognized. Their formation strongly depends on the reaction time and temperature and on amounts (thin film thicknesses) of Si and Ni which are on disposal for the reaction.

Preiskava reakcijskih produktov v termično obdelani večplastni strukturi Ni/Cr/Si

Ključne besede: polprevodniki, mikroelektronika, plasti tanke, strukture večslojne, difuzija, silicidi nikljevi, DSC kalorimetri diferencialni, AES Auger spektroskopija elektronska, TEM mikroskopija elektronska

Povzetek: Priprava dobro karakteriziranih večplastnih struktur s kontrolo difuzijskih procesov in reakcij na faznih mejah je posebnega pomena za proizvodnjo vezij v mikroelektroniki. Silicidi so našli široko uporabo v mikroelektroniki zaradi primernih električnih karakteristik in, ker skupaj z difuzijskimi barierami tvorijo termodinamično stabilne sisteme. V tem delu smo modelno večplastno strukturo Ni/Cr/Si, sestavljeno iz napršenih tankih plasti, debeline od 20 μm do 60 μm, ogrevali v diferencialno rastrskem kalorimetru (DSC). En vzorec večslojne strukture smo s hitrostjo 40° C/min ogrevali do 380°C in drugega do 550°C. Na svežih in termično izpostavljenih večplastnih strukturah smo s profilno analizo z metodo AES in presevno elektronsko mikroskopijo (TEM) ugotovili, da v termično obdelanih vzorcih močno reagirajo plasti niklja in silicija, medtem , ko je bila po pričakovanju reakcija med kromom in silicijem šibkejša. Identificirali smo dve vrsti silicidov, Ni_2S in NiSi, kateri od njiju nastane pa je razen od časa reakcije in temperature odvisno tudi od razpoložljivega silicija in niklja.

1.INTRODUCTION

Multilayer structures for microelectronics become thinner and more complex, being composed of individual thin films which may function as Schottky barriers,ohmic contacts, dielectrics, etc.(1,2). Silicides find widespread applications because they are compatible with standard integrated circuit processing, possess low electrical resistivity and acceptable thermodynamic stability (3,4). The formation of silicides in thin films of tipically some hundred nanometers (5,6) or for nearly bulk material (7,8) has been extensively studied with different techniques. Auger electron spectroscopy (AES) is a very useful method for the characterization of silicide thin films with a thickness of some ten nanometers or even less (9,10,11). A model multilayer structure composed of Ni, Cr and Si thin films with individual layer thicknesses between 20 nm and 60 nm has been developed(12), and in this work the reaction products formed by a thermal treatment of the multilayer during differential scanning calorimetry (DSC) measurements were studied. The silicides formation and structural changes due to interfacial reactions and diffussion processes in the Ni/Cr/Si multilayer were studied by DSC, AES and TEM investigations. The combination of all three mentioned techniques yielded a new insight on the type and extend of thermally activated interactions taking place in this ternary multilayer system.

2.EXPERIMETAL

The Ni/Cr/Si multilayer was sputter deposited onto smooth silicon (111) substrates in a Balzers sputron plasma chamber (12, 13). The multilayer consisted of twelve thin films with thicknesses given here in nanometers: Ni20/Cr20/Si20/Ni20/Cr20/Si50/Ni20/Cr20/Si60/Cr20/Ni20/Cr20/Si substrate, as shematically shown in Fig.1 and in Ref.12 (TEM micrograph in Fig.2,

Ref.12). After deposition, one sample was AES depth profiled before heat treatment in a Perkin-Elmer DSC-7 instrument. The other two samples were heated in an argon atmosphere at rates of 40°C/min from room temperature to 380°C and 550° C, respectively, and quenched with 340° C/min in a Perkin-Elmer DSC-7 instrument.

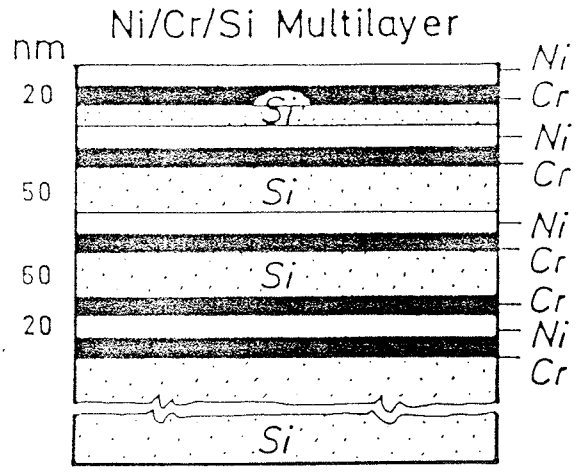

Fig. 1: Schematic cross-section of the sputter deposited Ni/Cr/Si multilayer

The samples were analysed with a Scanning Auger Microprobe (Physical Electronics Industries, SAM 545 A) at a base pressure in the vacuum chamber below 1,3 x 10^{-7} Pa. A primary electron beam of 3keV, 1μA and a diameter of about 50 μm was used. Sputter depth profiling was performed on stationary samples using two 1keV Ar^+ ion beams at an incidence angle of 47°. The Ar pressure was about 7,3 x 10^{-3} Pa and the samples were ion sputtered over an area not smaller than 4x4 mm. Auger peak-to- peak heights of Cr (529 eV), Ni (848 eV), Si (92 eV) and 0 (510 eV) were quantified in the AES depth profiles using the relative elemental sensitivity factors given in the PHI handbook (14). For structural and chemical investigations with a transmission electron microscope (JEOL 2000 FX) and energy - dispersive spectroscopy (EDS), the sample heated to 550°C were cross- sectioned and thinned by 6 keV Ar ion milling on a liquid nitrogen cooled cold stage to a thickness transparent for 200 keV electrons.

3. RESULTS AND DISCUSSION

The AES depth profile of as deposited Ni/Cr/Si multilayer shows the sharp interfaces, without the interdiffusion between the thin films (Fig.2a). This is in agreement with erlier depth profiling studies and TEM investigations (12). The other two depth profiles were obtained on the multilayers heated at rate of 40°C/min from room temperature to 380°C (Fig.2b) and 550°C (Fig.2c), respectively. In both profiles, considerable changes of the in-depth distribution of the elemental composition are recognized. The depth profile of the sample heated to 380°C shows that strong reactions between the nickel and silicon layers took place: the Ni from the fourth layer (from the top) reacted almost completely with the third Si layer of originally 20 nm thickness. Due to the thicker (sixth) silicon layer (50 nm) only about a half amount of the Si from this layer was consumed for the reaction with the adjacent seventh Ni layer. In both reacted regions the formed silicide has the nearly stoichiometric composition of Ni_2Si silicide. At 380°C, the ninth silicon layer near the substrate did not react with the neighbouring chromium layers due to the much lower diffusivity of chromium in silicon as compared with Ni and to the lower

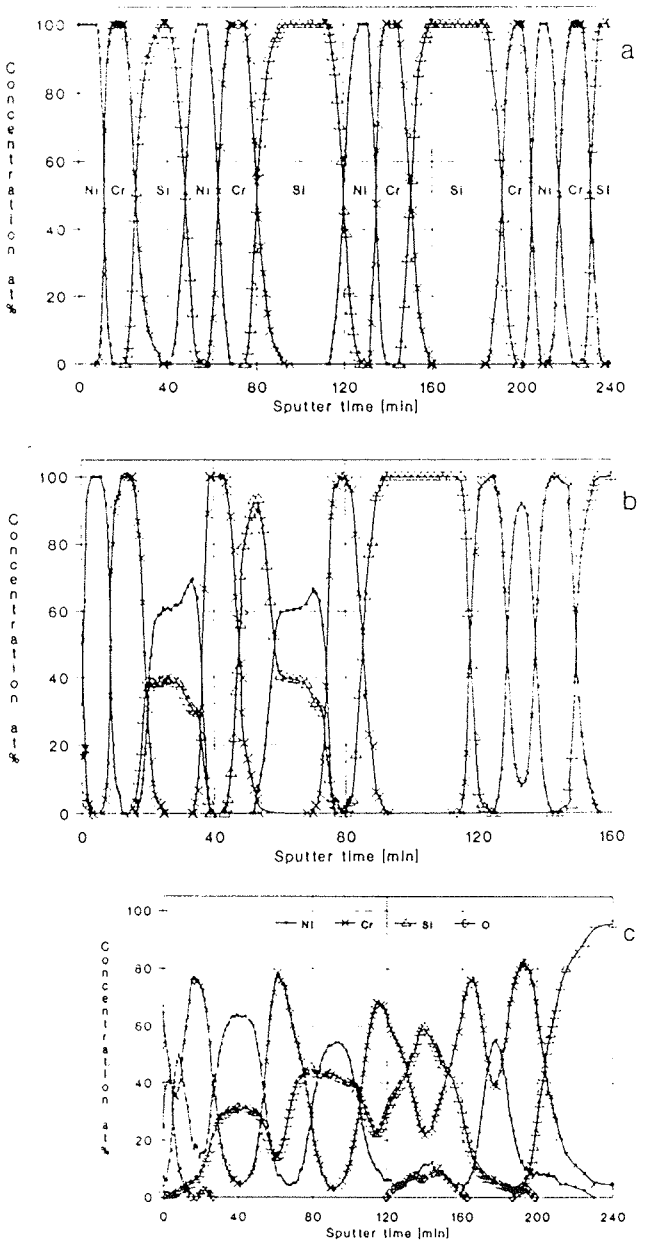

Fig. 2a,b,c: AES sputter depth profiles of the Ni/Cr/Si multilayers not subjected to heating (a) and after DSC heating at a rate of 40°C/min (b) to 380°C and (c) to 550°C.

formation enthalpy of chromium silicide (15). The concentration of chromium in the Ni thin film nearest to the substrate (Fig.2b) apparently shows the diffusion of chromium in the nickel layer. However, this interface broadening is mainly ascribed to the loss of depth resolution at the applied sputtering conditions (12) at the respective depth of the sample and not to diffusion processes.

As expected, the diffusion processes are more intensive in the Ni/Cr/Si multilayer heat treated to 550°C. In this case end silicon layers reacted completely with the neighbouring Ni layers resulting in two different silicides (Fig.2c). In the region close to the surface, mainly the Ni_2Si was formed and in the region in the middle of the multilayer, where a larger amount of silicon was on disposal, the NiSi with some excess of Ni was found (Fig.2, at a sputtering time of about 90 minutes). Both silicides were confirmed with two other methods: with EDS analysis of the mentioned regions on a cross-sectioned, heat treated Ni/Cr/Si multilayer shown in Fig.3

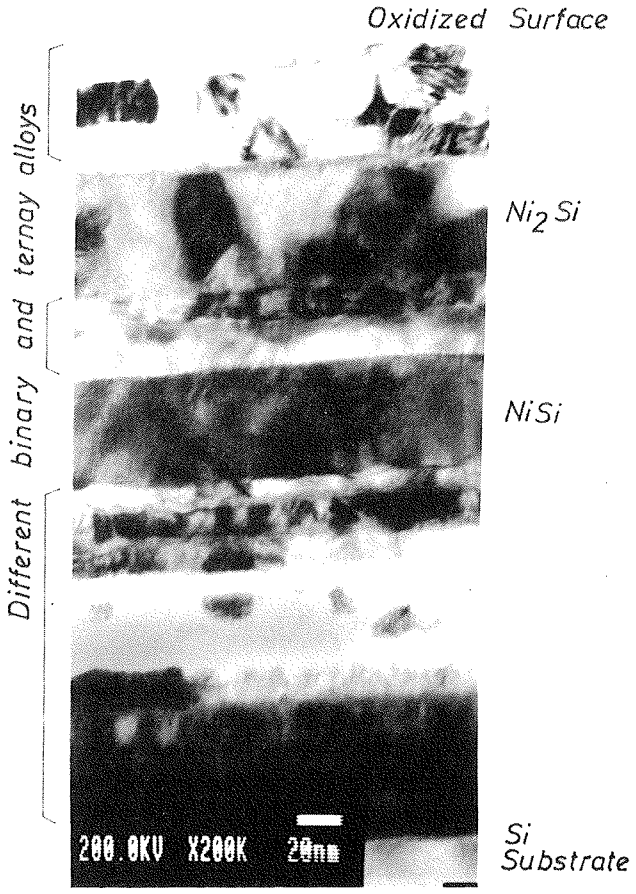

Fig. 3: Bright field TEM image of the Ni/Cr/Si multilayer after heating at a rate of 40°C/min from room temperature to 550°C with marked regions of Ni silicides. For a detailed explanation of the other reacted regions see the Ref. 20.

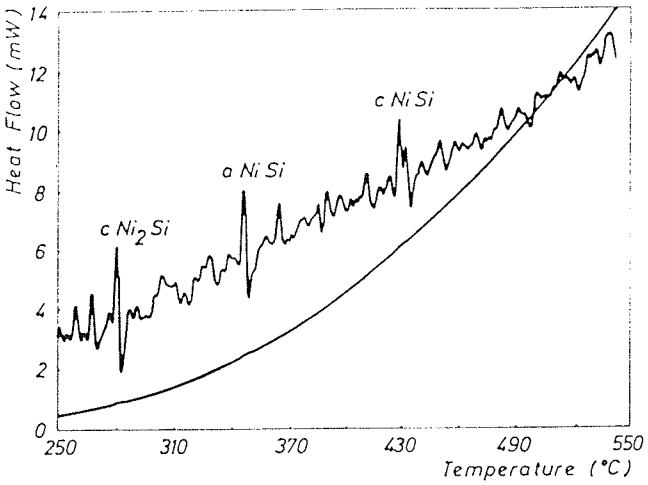

Fig. 4: DSC trace for the Ni/Cr/Si multilayer heated at scan rate of 40°C/min (the lower curve) and its respectively first derivate (the upper curve) with the peaks attributed to the formation of crystalline Ni_2Si, amorphous NiSi and to the growth of crystalline NiSi.

and with DSC measurement from room temperature to 550°C (Fig.4). The first derivate of the DSC trace in Fig.4 shows three typical peaks which can be attributed to the formation of crystalline Ni_2 Si, amorphous NiSi (11,16,17,18,19) and to the growth of crystalline NiSi. In the sample heated to 550°C, the diffusion of Cr in Ni layers and interfacial reactions between Si and Cr took place and the formation of Cr silicides started too. However, probably due to exothermical and endothermical reactions occuring at the same time and due to a small amount of reaction products, the Cr silicides cannot be recognized by DSC measurements, and the AES and TEM investigations are more convincing for the identification of small reacted regions and broadened interface regions where binary and ternary solid solutions were present (20).

4. CONCLUSIONS

The combination of DSC, AES and TEM investigations was used to study the interfacial reactions, diffusion processes and silicides formation in the thermally treated Ni/Cr/Si multilayer structure. In the sample heated in a DSC instrument at rate of 40°C/min from room temperature to 380°C the reaction between Ni and Si results in the formation of Ni_2Si. The heat treatment of the multilayer to 550°C accelerated the reaction between Ni_2Si and Si resulting in NiSi silicide, and the diffusion processes between Si and Cr and Cr and Ni were also observed. However, the reaction regions with small amount of Cr silicide and broadened interface regions with a composition corresponding to binary and ternary solid solutions can be recognized from AES depth profiles and TEM investigations only, and cannot be disclosed with DSC measurements. The type of the formed Ni-silicide (Ni_2Si or NiSi) depends beside the reaction

time and temperature also on the amounts of Si and Ni which were available for the reaction.

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