Egyetemi doktori (PhD) értekezés tézisei

Investigation of diffusion and diffusion controlled processes in metal/semiconductor nanolayers by SNMS technique

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Introduction

Enormous attention has been paid to the investigation of diffusion (intermixing) effects between semiconductor layers and contact materials used in microelectronic devices in the past 40 years.

The reasons of the intermixing can be found in the origin of these devices. They are multilayered systems, prepared artificially and have significant free energy: thus they can transform easily by diffusion and solid state reaction processes. The research and investigation of the intermixing controlled processes are timely problems from the standpoint of the continuous miniaturization of microelectronic devices as well (eg. shorter and shorter diffusion paths, changes in the kinetics).

Modern depth profiling methods (SIMS, SNMS, AES combined with ion sputtering) are sensitive enough to map concentration profiles formed in thin film systems with good depth resolution. These in-depth profiles afford possibility for evaluating various diffusion

coefficients and observing solid-state reactions near the interfaces.

Aims

Preparation of different types of metal/semiconductor layered systems by magnetron sputtering and, after heat treatments, their investigation by Secondary Neutral Mass Spectrometry were my main objects. On the basis of data obtained a detailed analysis of the diffusion processes and diffusion controlled solid state reactions was also possible.

My works were:

- Investigation of the properties and thermal stability of diffusion barriers applied between silicon and copper layers.
- Evaluating grain-boundary and effective interdiffusion coefficients from SNMS concentration-depth profiles in metal/semiconductor systems.
- Examination of kinetics of solid-state reactions and interface shifts by SNMS technique.

Results

1. Thermal stability and degradation of tantalum and tantalum-pentoxide diffusion barriers were investigated between Si and Cu layers.

Si/Ta/Cu/W; Si/Ta_2O_5/Cu/W; Si/Ta-Ta_2O_5/Cu/W systems were prepared by magnetron sputtering and annealed in vacuum from 473 to 1023 K. The changes were followed by SNMS technique.

a. No changes were found in the concentration profiles after annealing at 623 K in Si/Ta10nm/Cu25nm/W10nm samples. Above 623 K the tantalum atoms start to migrate through the copper layer and appear at the Cu/W interface. After annealing at 823 K silicon atoms also start to diffuse through the Ta and Cu layer.

b. Annealing the Si/$Ta_2O_5$10nm/Cu25nm/W10nm layers at 823 K and above it, the diffusion of silicon atoms through the Ta_2O_5 layer and the re-crystallization of Ta_2O_5 layer were observed. At this temperature the silicon atoms migrate through the new nano-crystalline Ta_2O_5 and Cu layer, furthermore appear at the Cu/ Ta_2O_5 and Cu/W interface.

c. In the Si/Ta5nm-$Ta_2O_5$5nm/Cu/10nm/W10 nm system we found that it has relatively high thermal stability. Below 1000 K no changes were found in the samples. At higher temperature the intermixing controlled degradation is caused by the diffusion of silicon atoms through the bi-diffusion barrier. The higher thermal stability of this layer structure can be explained by the continuous oxidation of the Ta layer. Between the Ta and Ta_2O_5 layer through the annealing a new metastable Ta_xO_y layer can be observed. This amorphous product layer does not contain diffusion short-circuits (e.g. grain-boundaries).

2. Grain-boundary diffusion Ta atoms were investigated in Si/Ta/Cu/W nano-layered systems in „C" kinetic diffusion regime. After preparing and annealing the samples the changes in the SNMS concentration profiles were analysed. From the concentration profiles diffusion coefficients and their activation energy were also evaluated.

a. From the heat treatments of the samples at 593 K for 1, 3 and 6 hours the fast diffusion of Ta atoms

through the Cu layer and their accumulation at the Cu/W interface was detected. At this temperature the segregated Ta atoms spread out by interface diffusion at the Cu/W interface. After this interface diffusion these atoms act as a secondary diffusion reservoir for back diffusion into the Cu layer.

b. From the observation of the first appearance of the Ta atoms at the Cu/W interface, grain-boundary diffusion coefficient was estimated. ($D_{gb}=10^{-19}$ m^2/s). This value belongs to the diffusion of Ta atoms along the Cu's fastest diffusion pathses.

c. From the intermixing at the Ta/Cu interface, taking place between 473 and 773 K the effective interdiffusion coefficients were calculated using the „Central-gradient" method. From the values the activation energy of this process was also estimated. (Q=100 kJ/mol).

d. The segregation factor of Ta in Cu grain-boundaries was also estimated from the grain-size (obtained from TEM picture) in the Cu layer.

e. For the explanation of these results a grain-boundary diffusion model was created in the

substrate/diffusant/thin-film/cap-layer system for “C” kinetic diffusion regime. At first, the atoms of the diffusant (source) layer migrate through the fastest “GB”-s and the triple-junctions of the thin-film to the thin-film/cap-layer interface. After their segregation at this interface they act as secondary diffusion source for back diffusion into the thin film layer. Later on the thin film was gradually filled up with the diffusing atoms and composition depth profiles, determined by SNMS, showed a maximum at the cap layer-thin film interface. These observations can be interpreted supposing a bimodal grain-boundary structure with different (fast and low) diffusivities.

3. Applying the above model and profile fitting methods on Si/Co150nm/Ta10nm system, I could evaluate different types of diffusion coefficients. After calculating the concentration-depth profiles from the intensity-sputtering time data base, properties of silicon atom transport through the nano-crystalline Co layer were analysed.

a. Similarly to point 2e the silicon atoms diffuse through the Co layer and accumulate at the Co/Ta interface inducing back diffusion into the Co layer.

b. From the first appearance of Si atoms at the Co/Ta interface grain-boundary diffusivities were estimated at 3 different temperatures. At 473, 553 and 583 K these values are: $4*10^{-20}$, $1{,}5*10^{-18}$ and $3*10^{-18}$ m^2/s respectively.

c. From intermixing at the Co/Si interface effective-interdiffusion coefficients between 473 and 623 K were calculated by the “CG-method”. The activation energy of this process was evaluated as well. (Q=120 kJ/mol).

4. Investigations of solid-state reactions and interface shifts in Si/a-Si150nm/Ni50 nm systems were carried out using SNMS instrument in combination with profilometer measurements. We could follow both the shrinkage and growth of layers i.e. the movements of individual interfaces was determined.

a. After sample preparation and heat treatments the changes in the layered structure were mapped by Secondary Neutral Mass Spectrometry. I measured the

distance of the layers from the surface either in the as-deposited or in the annealed sample after the SNMS measurements by profilometer. Using this method the shrinkage of nickel and amorphous silicon layers and the growth of the reaction layer (Ni_xSi_{1-x}) between the Ni and Si layers can be obtained as the function of annealing time at fixed temperature (503 K).

b. The rate of the growth and shrinkages for shorter annealing times followed linear kinetics (k_c=1), for longer annealing time they turned into parabolic kinetics (k_c=0.5).

c. From resistance measurements, carried out at 503 K, it was obtained that the resisitivity of the samples first increased and, after a plateau, it started to decrease and reached a constant resistance value. We concluded that at first an amorphous and high resistivity phase grows and then a crystallization processes take place.

d. With XRD measurement carried out on the sample annealed at 503 K for 1620 min we identified the crystalline phases in the reaction layer (Ni_xSi_{1-x}: NiSi and Ni_2Si).

e. From the SNMS concentration-depth profile we could show that the layers forming between the Ni and Si layers are first a NiSi phase with composition of 50:50 atomic % formed and later the Ni_2Si (with 66:33 atomic %) appeared either.

Papers

[K1] **A. Lakatos**, A. Csik, G.A. Langer, G. Erdelyi, G.L. Katona, L. Daroczi, K. Vad, J. Toth, D.L. Beke *Investigations of failure mechanisms at Ta and TaO diffusion barriers by secondary neutral mass spectrometry*, **Vacuum,** Volume 84, Issue 1, 25 August 2009, Pages 130-133

[K2] **A. Lakatos**, G. Erdelyi, G.A. Langer, L. Daroczi, K. Vad, A. Csik, A. Dudas, D.L. Beke : *Investigations of diffusion kinetics in Si/Ta/Cu/W and Si/Co/Ta systems by secondary neutral mass spectrometry*, **Vacuum,** Volume 84, Issue 7, 4 March 2010, Pages 953-957

[K3] **A. Lakatos**, G. A. Langer , A.Csik, C. Cserhati , M. Kis-Varga, L. Daroczi, G.L. Katona,
Z. Erdélyi, G. Erdelyi, K. Vad, D. L. Beke *Method for the investigation of nanoscale shift of individual interfaces by Secondary Neutral Mass Spectrom*etry **Applied Physics Letters** 97, 233103 (2010)

[K4] **A. Lakatos**, G. Erdelyi, A. Makovec, G. A. Langer , A.Csik, K. Vad, D. L. Beke *Investigation of diffusional intermixing in Si/Co/Ta system by Secondary Neutral Mass Spectrometry*, **Vacuum,** submitted

[K5] D.L. Beke, **A. Lakatos**, G. Erdelyi, A. Makovecz, G. A Langer, L. Daroczi, K. Vad, A. Csik: *Investigation of grain boundary diffusion in thin films by SNMS technique*, **Def. Diff. Forum**, in print

Citations

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Presentations

[E1] **A. Lakatos**, G. Erdelyi, G.A. Langer, L. Daroczi, K. Vad, A. Csik, A. Dudas, D.L. Beke: *Investigations of diffusion kinetics in Si/Ta/Cu/W and Si/Co/Ta systems by secondary neutral mass spectrometry* 4-th Symposium on Vacuum based Science and Technology in conjunction with 8-th Annual Meeting of German Vacuum Society (DVG) 20-23. Szept. 2009 Kolobrzeg, Poland

Posters

[P1] A. Lakatos, G. Erdelyi, A. Makovec, G. A. Langer , A.Csik, K. Vad, D. L. Beke *Investigation of diffusional intermixing in Si/Co/Ta system by Secondary Neutral Mass Spectrometry* 13th Joint Vacuum Conference, 21-25. June 2010. Poprad, Slovakia

[P2] A. Lakatos, A. Csik, G.A. Langer, G. Erdelyi, G.L. Katona, L. Daroczi, K. Vad, J. Toth, D.L. Beke *Investigations of failure mechanisms at Ta and TaO diffusion barriers by secondary neutral mass spectrometry* 12th Joint Vacuum Conference, 10th European Vacuum Conference,7th Annual Meeting of The German Vacuum Society 22-26. September.2008, Balatonalmadi, Hungary

[P3] A. Csik, K. Vad, G. A. Langer, **A. Lakatos** : *Depth profiling and composition analysis by Secondary Neutral Mass Spectrometry.* 7th European Workshop on Secondary Ion Mass Spectrometry. Münster, Germany, 19-21 Sept., 2010