



Investigations of diffusion kinetics in Si/Ta/Cu/W and Si/Co/Ta systems by secondary neutral mass spectrometry

A. Lakatos^{a,*}, G. Erdelyi^a, G.A. Langer^a, L. Daroczi^a, K. Vad^b, A. Csik^b, A. Dudas^c, D.L. Beke^a

^a University of Debrecen, Department of Solid State Physics, H-4010 Debrecen, P.O. Box 2, Hungary

^b Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, P.O. Box 51, Hungary

^c Semilab Semiconductor Physical Laboratory, H-1117 Budapest, Prielle Kornélia Street 2, Hungary

A B S T R A C T

Keywords:

Co and Cu interconnection technology
Interface segregation
Ta diffusion in Cu
Si diffusion in Co
Centre-Gradient method

Proper understanding of the degradation mechanisms and diffusion kinetics of copper and cobalt interconnections for advanced microelectronics is important from the point of view of fundamental research and technology as well. In this paper Si(substrate)/Ta(10 nm)/Cu(25 nm)/W(10 nm) and Si(substrate)/Co(150 nm)/Ta(10 nm) samples, prepared by DC magnetron sputtering, were investigated. The samples were annealed at several temperatures ranging from 423 K to 823 K for various times. The composition distributions were detected by means of Secondary Neutral Mass Spectrometry (SNMS). Microstructural characterization of samples was carried out by means of Transmission Electron Microscopy (TEM). It is shown that the changes in the composition profiles were mainly caused by grain boundary, GB, diffusion and the effective GB diffusion coefficients of Ta in Cu were determined both by the “first appearance” and “centre-gradient” methods. The activation energy is 100 kJ/mol. The importance of the Ta penetration into the Cu and its accumulation at the Cu/W interface can lead to an increase of the Ta content in the copper film. This can be an important factor in the change/degradation of the physical parameters (e.g. the electrical resistance) of interconnects. Furthermore a Ta segregation factor in Cu was evaluated. Preliminary results in the Si(substrate)/Co(150 nm)/Ta(10 nm) indicate fast (GB) diffusion of the Si into the Co layer, formation of a cobalt silicide layer at the Co/Si interface and Si accumulation first at the Ta/Co interface and later a retarded accumulation at the free Ta surface.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Investigation of copper and cobalt interconnection technology for advanced microelectronics in the ultimate large scale integration is important to extend the lifetime of the microelectronic devices [1–5]. Films of Ta and Ta alloys proved to be a good diffusion barrier layer to prevent mixing of contact (cobalt) and interconnect (copper) layers. This is based on their high melting points, lack of reactivity with Cu and relatively good adhesion to SiO₂ [6]. Discussions of barrier properties and failure mechanism for Ta and its compounds can be found in references [7–11]. In contrast to these papers we present detailed investigation of the Ta diffusion and changes in the Ta composition of the Cu film in the Si/Ta/Cu/W system. Diffusion kinetics and segregation phenomena were followed by Secondary Neutral Mass Spectrometry (SNMS, type: INA-X, SPECS GmbH, Berlin) and were investigated by transmission electron microscopy (TEM, type: JEOL 2000 FX + EDS). Preliminary measurements on the

diffusion intermixing in the Si(substrate)/Co(150 nm)/Ta(10 nm) samples were also carried out at 583 K.

2. Experimental

The Ta/Cu/W films were deposited onto (111) oriented p-type silicon substrates by DC magnetron sputtering at room temperature. The base pressure of the sputtering chamber was lower than 2×10^{-5} Pa. Circular Ta, Cu, W targets, 2 in. diameter, were used as sputtering sources. During tantalum, copper and tungsten layer deposition, the Ar (99.999%) pressure (under dynamic flow) and the sputtering power were 5×10^{-1} Pa and 40 W, respectively. The sputtering rates were calculated from the layer thickness measured by an AMBIOS XP-1 profilometer. A tungsten cap layer was applied in order to avoid the sample oxidation and to keep the out-diffused tantalum inside the sample during the heat treatments. All samples were annealed under vacuum (3×10^{-5} Pa) at temperatures 473 K, 593 K, 673 K, 723 K and 773 K for 60 minutes. The time evolution of the process was studied at 593 K, the annealing times were 0.66, 3 and 6 hours. In each annealing process, a new, individual sample was used.

* Corresponding author.

E-mail address: alakatos@dragon.unideb.hu (A. Lakatos).

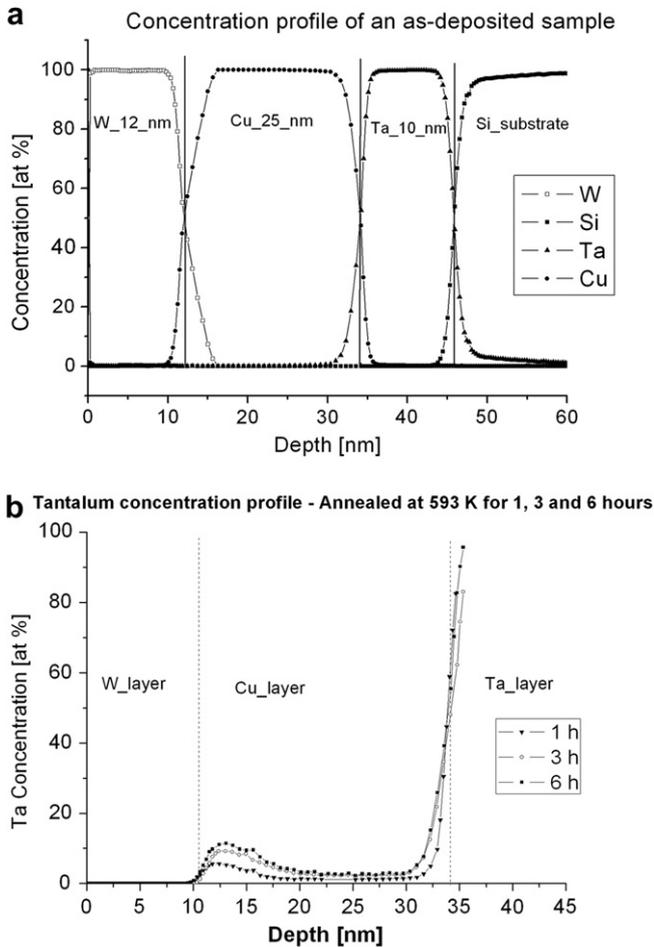


Fig. 1. a: Concentration profile of the as-deposited Si(substrate)/Ta(10 nm)/Cu(25 nm)/W(10 nm) sample. b: Ta concentration profile after 1, 3 and 6 hours annealing at 593 K.

The microstructure of samples was analyzed by TEM. The concentration–depth profiles were detected by SNMS (INA-X, SPECS GmbH, Berlin). This instrument 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) [12]. In this case the detection limit of the SNMS is about 10 ppm. Details of quantification procedure of SNMS spectra are described in [13,14].

3. Results and discussion

In contrast to other papers [8,15] where the authors focused on the Cu and Si diffusivity in the barrier layer (Ta), as well as on the Tantalum diffusivity in Si, we detected the Ta diffusion through the Cu layer. Furthermore, the mixing process at the Ta/Cu interface was also observed. Fig. 1a shows the concentration profiles measured in the as-deposited samples. It can be seen that the initial W/Cu interface is much less sharp than the Cu/Ta and especially than the Ta/Si one. This is most probably due to the increasing roughness of the interfaces with increasing distance from the Si substrate (see also later in the TEM micrograph), caused by the deposition technique. This results in a smeared region on the depth profiles. The effect of a low temperature annealing (at 593 K) can be observed in Fig. 1b: Ta atoms migrate through the Cu layer, appear and accumulate at the W/Cu interface. It is worth nothing that there exist a small asymmetry in the W/Cu and Ta/Cu interfaces (the

profile is always sharper in the high melting point material, i.e. in W and Ta). This can be a manifestation of asymmetric diffusion [14]. However the bulk diffusion coefficients are too small to cause this nm wide penetrations and thus only the grain-boundary diffusion in Cu, during the room temperature deposition, can be the responsible for. Furthermore, the asymmetry at the W/Cu interface can also be caused by a “dynamic” segregation effect (see e.g. [16]); during the deposition of W onto the surface of Cu the Cu atoms tend to climb up to the building W layer.

The observed appearance of the Ta at the W/Cu interface offers a good opportunity to estimate the Ta grain boundary diffusivity in Cu by the “first appearance method” [17]. Using the annealing parameters, and assuming “C-type” GB kinetic regime ($D \cong h^2/4t$, where h is the thickness of the Cu film) we deduced $D = 10^{-19}$ m²/s for the Ta GB diffusion coefficient at 593 K. This value can be interpreted as an order of magnitude estimate of the grain boundary diffusion coefficient along triple junctions i.e. diffusion along the fastest GB diffusion paths [18,19]. Indeed the first Ta atoms will arrive at the Cu/W interface by diffusion along GB's with the highest diffusivities.

Interestingly, Ta atoms start to accumulate at the Cu/W interface (Fig. 1b.). This accumulation is also enhanced by the high melting point of W: at this temperature practically no penetration of Ta/Cu is expected into W. The kinetics of this interface segregation is obviously influenced by the GB structure of the film too. The segregated amount of the Ta can act as a diffusion source for back diffusion along GB's with slower diffusivity: this effect can lead to an overall increase of the amount of the Ta in the Cu layer.

In addition to the previous results, effective grain-boundary diffusion coefficients of Ta can also be determined from composition profiles obtained at the Cu/Ta interface using the so called ‘centre-gradient’ method [20]. This method takes into account that the composition profile can have an initial, finite distribution. The concentration–depth profile of the as-deposited specimen obtained by SNMS sputter-depth profiling is smeared out due to the following effects a) roughness of the original interface, b) the mixing process during the deposition (segregation, diffusion) (Fig. 1a), c) instrumental effects of the SNMS profiling. Accordingly, the concentration profile measured after heat treatment has to be considered as a convolution of the profile due to diffusion with a resolution function determined from the concentration profile of the as-deposited specimen [20]. If the concentration changes can be described by one effective diffusion coefficient and it has negligible composition dependence around the interface composition, then the concentration profiles have a complementary error function dependence on depth near the interface:

$$c(y, t) = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{y}{2\sqrt{Dt}} \right) \right], \quad (1)$$

where y is the distance (depth) from the initial interface and t is the annealing time. Under the above conditions both measured

Table 1
Diffusion coefficients and the calculated errors from “Centre – Gradient” method.

Annealing temperature of Si/Ta/Cu/W (K)	Annealing time (hours)	D Ta from CG method (m ² /s)	Error \pm (m ² /s)
473	1	4,71E–24	3,15E–23
593	1	6,31E–23	5,24E–23
593	3	4,98E–23	1,61E–23
593	6	1,45E–23	1,23E–23
673	1	1,66E–22	1,87E–23
773	1	4,33E–22	1,16E–22
823	1	7E–22	2,63E–22

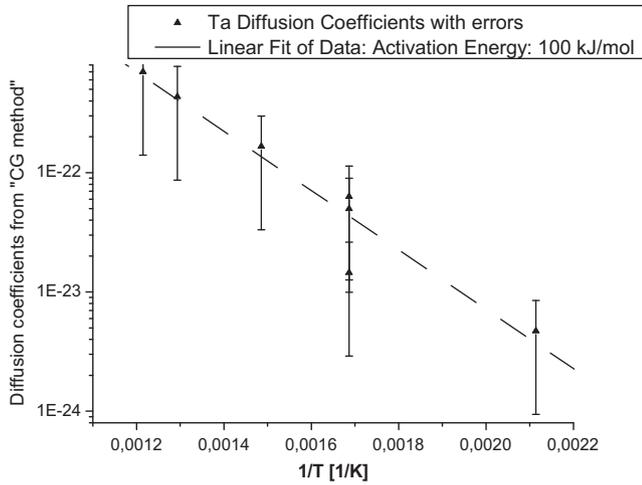


Fig. 2. Arrhenius diagram of Ta diffusivities with activation energy.

concentration profiles, before and after annealing, obey Eq. (1) near the interface and the interdiffusion coefficient can be determined from the following formula:

$$\tilde{D} = \frac{1}{4\pi G_0^2 t} \left[\left(\frac{G_0}{G_t} \right)^2 - 1 \right], \quad (2)$$

where G_0 and G_t are the concentration gradients at the interfaces obtained for the as-deposited and annealed (for time t) specimens, respectively [16,19]. Thus using this ‘centre-gradient’ method the Ta diffusion coefficients at the Cu/Ta interface have been calculated (Table 1). In Table 1 the estimated errors of the diffusivities are also presented. It is worth mentioning that the diffusion coefficients measured at 593 K show time dependence: the evaluated Ta diffusion coefficients decrease with time. The Arrhenius plot of the Ta diffusion coefficients is shown in Fig. 2. The activation energy was found to be about 100 kJ/mol, which is about the half of the activation energy for Cu bulk self-diffusion measured in low temperature regime $Q_0 = 203,6$ kJ/mol [21]. This fact confirms that the obtained effective diffusion coefficients are GB diffusion coefficients. The deviation of the absolute value of these from 10^{-19} m²/s, obtained at 593 K from “first appearance” method can be understand by taking into account the different diffusivities along different Gb’s. The interface intermixing at the beginning is controlled by the transport along fastest Gb paths (triple junctions) and with increasing time the composition profile more and more includes contributions from transport along slower GB’s as well (Fig. 3). Thus the effective GB diffusion coefficient of intermixing decreases with increasing time (see the values at 593 K in Table 1.) and all of them is smaller than the value belonging to the number calculated from the first appearance.

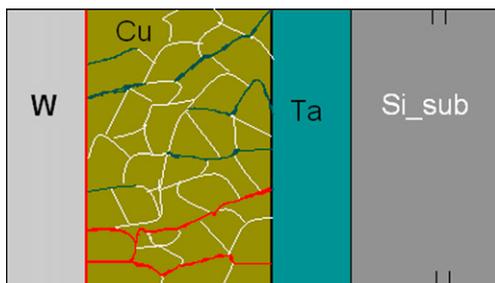


Fig. 3. Sketch of different grain boundary diffusion paths in Cu: red and blue are fast and “normal” paths, respectively.

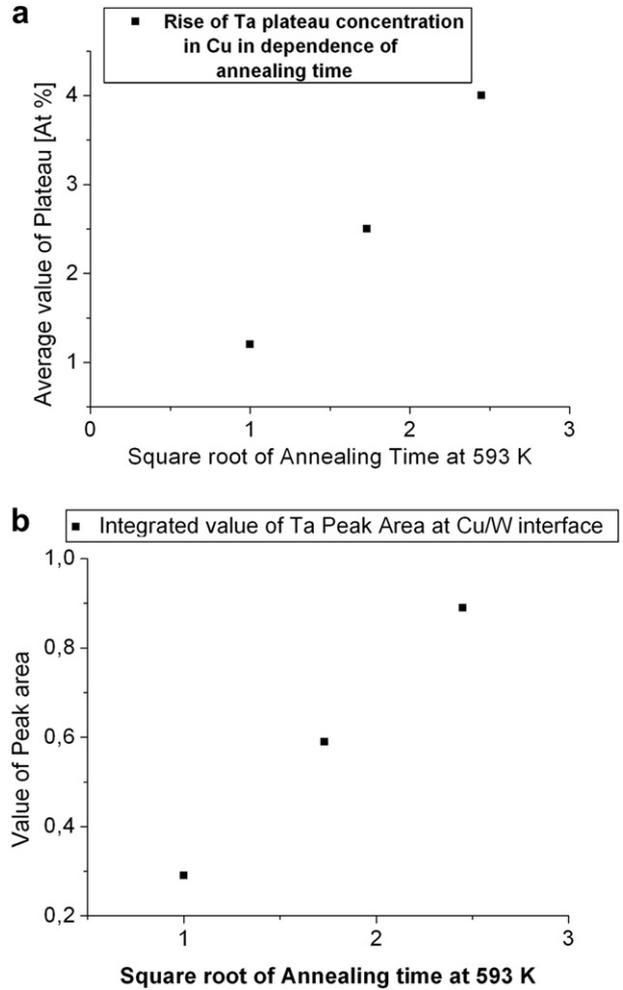


Fig. 4. a: Time dependence of Tantalum concentration as a function of annealing time at the bottom of the profile in Cu. b: Time dependence of the area of the Ta concentration peak at the Cu/W interface.

It is feasible to estimate the Ta segregation factor in Cu from the measured Ta depth profiles. In the literature there are reliable radiotracer volume self-diffusion data available for Cu in the temperature range of our measurements [21]. Though Ta tracer

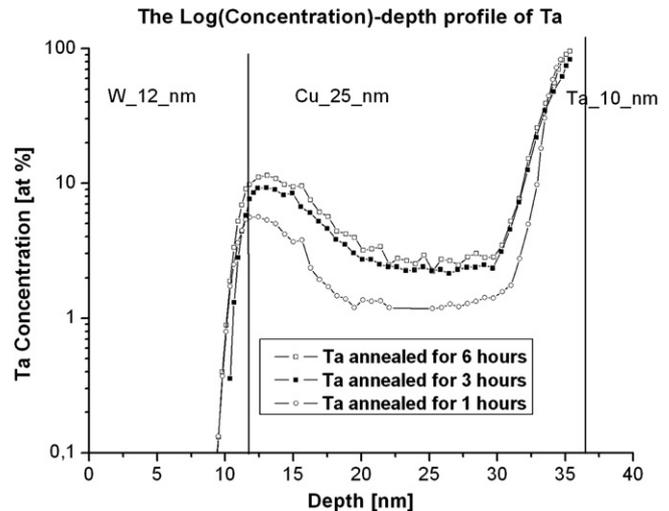


Fig. 5. Ta composition profile: pay attention to the asymmetry of the interfaces.

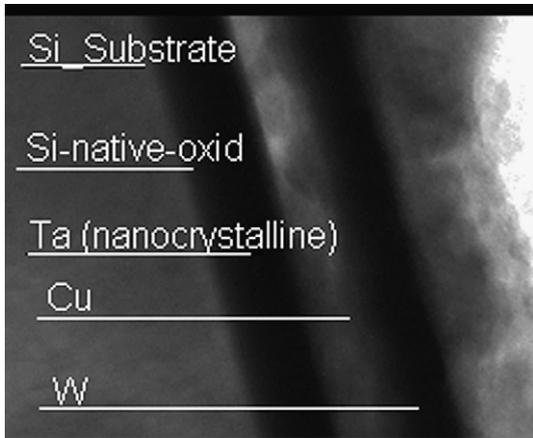


Fig. 6. TEM picture of the sample Si/Ta/Cu/W after anneal at 593 K for 1 h.

volume diffusion data in Cu are missing, the Cu volume self-diffusion coefficient can be considered to be a good upper limit for Ta impurity volume diffusion in Cu at a given temperature. The estimated Ta diffusion coefficient is about $1.45 \times 10^{-23} \text{ m}^2/\text{s}$ at 593 K. The volume penetration depth for 1 h annealing time is about 0.5 nm, comparable with the grain boundary width. The volume fractions of the grain boundaries and the Ta-penetrated layer of grains are approximately 5%, supposing a grain size of 10 nm in Cu. Assuming a reasonable low value for the Ta solubility (0.01%, 100 ppm), the measured average Ta concentration (4%) can be deduced if the Ta grain boundary concentration is about 80%. From this rough estimation one can get a value of 8000 for the Ta segregation factor in Cu.

Regarding the average composition of Ta in Cu the following conclusions can be drawn:

- The average Ta concentration (plateau) in the middle of Cu layer is increasing with time, after of 6 hours annealing it is approximately 4% (Fig. 4a);
- The Ta concentration peak area and its width (measured at the W/Cu interface) are also increasing with time (Fig. 1b);
- Both the time dependence of the plateau concentration and the peak area show a \sqrt{t} type time dependence (Fig. 4a, b);

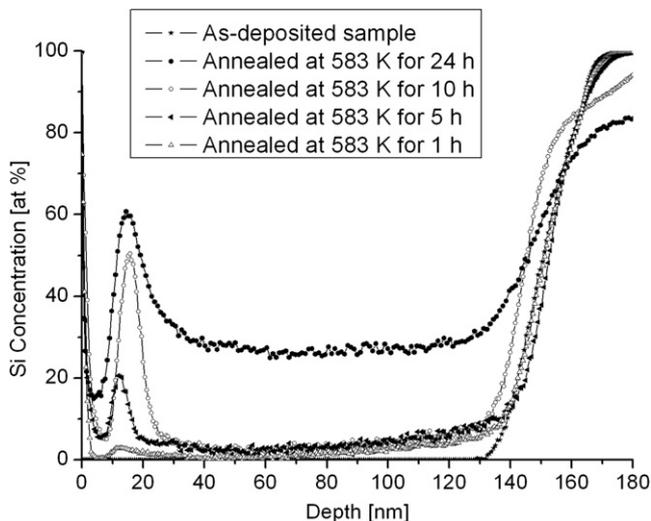


Fig. 7. Silicon concentration profiles for as-received sample and 4 annealed samples (at 583 K for 1, 5, 10 and 24 hours, respectively) in Si/Co/Ta system.

- A rough estimation of the grain boundary Ta concentration and segregation factor shows that that majority of Ta atoms are in the grain boundaries and the intermixing at the Cu/Ta interface is governed by grain boundary diffusion.

Finally, the observed asymmetry of the Ta profile, i.e. the Ta/Cu interface remains much sharper than the W/Cu interface, needs some comments. We recall that the depth resolution of the SNMS is less than 2 nm, the observed spatial extension of the accumulation peak is about 6–8 nm (Fig. 5). A similar spatial extension could be expected at the Ta/Cu interface due to the diffusion along grain boundaries. In order to reveal some structural and morphological properties of the interfaces we took some TEM pictures of the sample heat treated at 593 K for 1 h (Fig. 6). TEM investigation confirmed our picture deduced from SNMS profiles: the Ta/Cu interface is sharp; the W/Cu interface is rougher. This can be the main reason of the asymmetry observed together with aforementioned effect of the back diffusion along GB's with slower diffusivity from the segregated Ta layer: these effects can lead to an overall increase of the amount of the Ta in the Cu layer. The Ta segregation factor in Cu was estimated also, its value is about 8000.

3.1. Preliminary results measured in Si/Co/Ta system

In this system the samples were annealed at several temperatures ranging from 473 K to 673 K, between 1 and 24 hours. A fast transport of silicon atoms through the Co layer can be observed (Fig. 7), which leads to a gradual increase of the overall Si content in the Co film. Most probably this, similarly to the Ta diffusion in the Cu layer in the previous set of samples, is the result of Si GB diffusion. At the same time here the Si accumulates at the Co/Ta interface, which can be enhanced also by the fact that the diffusion in the high melting point Ta is much slower than in Co. It can also be seen that Ta serves as a moderate diffusion barrier: the Si accumulation on the free surface of the Ta is retarded, but takes place. The surface peak increases, while the peak at the Ta/Co interface (after a fast accumulation period) decreases. Further measurements are in progress and the results of detailed evaluation of the kinetics will be published elsewhere.

4. Conclusion

Our investigations carried out in Si/Ta/Cu/W and Si/Co/Ta systems, are based on SNMS depth profiling technique. In contrast to previous studies, we focused our investigation on the Ta (barrier material) transport in/into the Cu layer. We detected a fast Ta transport through the Cu grain boundaries and an accumulation of Ta at the W/Cu interface. Using the 'First appearance method' we estimated the Ta grain boundary diffusivity along the fastest grain boundaries at 593 K. At longer annealing times the average Ta concentration in the Cu film may increase up to about 4%, causing an increase of the resistivity of the interconnection layer. Using the 'Central-Gradient' method effective diffusion coefficients were estimated in the temperature range of 473–773 K, with an activation energy 100 kJ/mol. The activation energy shows that the intermixing at the Ta/Cu interface is mainly controlled by grain boundary diffusion. The observed asymmetry of the Ta profile is explained mainly in terms of the morphological differences of the interfaces. In the Si/Co/Ta system fast (GB) diffusion of the Si into the Co layer, formation of a cobalt silicide layer at the Co/Si interface and Si accumulation first at the Ta/Co interface and after some time a retarded accumulation at the free Ta surface were observed.

Acknowledgements

The authors gratefully acknowledge the support of the Hungarian Scientific Research Fund (OTKA) through Grants K 61253 and Foundation Universitas.

References

- [1] Erdélyi G, Langer G, Nyéki J, Kövér L, Tomastik C, Werner WSM, et al. *Thin Solid Films* 2004;459:303–7.
- [2] Hübner R, Hecker M, Mattern N, Hoffmann V, Wetzig K, Wenger Ch, et al. *Thin Solid Films* 2004;458:237–45.
- [3] Hoo-Jeong L, Kee-Won K, Changsup R, Sinclair R. *Acta Mater* 1999;47:3965–75.
- [4] Stolt L, d'Heurle FM. *Thin Solid Films* 1990;189:269.
- [5] Cros A, Aboelfotoh MO, Tu KN. *J Appl Phys* 1990;67:3328.
- [6] Lakatos A, Csik A, Langer GA, Erdélyi G, Katona GL, Daroczi L, et al. *Vacuum*; 2009.
- [7] Fischer D, Scherg T, Bauer JG, Schulze H-J, Wenzel C. *Microelect Eng* 2000;50:459–64.
- [8] Fang JS, Hsu TP, Ker ML, Lee JH, Hso CS, Yang LC. *J Phys Chem Solids* 2008;69:430–4.
- [9] Moshfegh AZ, Akhavan O. *Mater Sci Semiconduc Process* 2003;6(4):165–70.
- [10] Lee Yoon-Jik, Suh Bong-Seok, Park Chong-Ook. *Thin Solid Films* 1999;357:237–41.
- [11] Zhao C, Tókei Zs, Haider A, Demuynck S. *Microelect Eng* 2007;84:334.
- [12] Oechsner H. *Nucl Instru Methods Phys Res* 1988;B33:918–25.
- [13] Müller KH, Oechsner H. *Mikrochim Acta (Wien) Suppl* 1983;10:51–60.
- [14] Oechsner H, Getto R, Kopnarski M. *J Appl Phys* 2009;063523:105.
- [15] Loh SW, Zhang DH, Li CY, Liu R, Wee ATS. *Thin Solid Films* 2004;462–463:240–4.
- [16] Labat S, Gerguad P, Thomas O, Gilles B, Marty A. *Appl Phys Lett* 1999;75:914–6.
- [17] Hall PM, Morabito JM. *Surf Sci* 1976;59:624.
- [18] Rabukhin VB, Panikarski AS. *Poverhnost*; 1986:150.
- [19] Bokstein B, Ivanov V, Oreshina O, Peteline A, Peteline S. *Mater Sci Eng* 2001;302(1):151–3.
- [20] Chakraborty J, Welzel U, Mittemeijer EJ. *J Appl Phys* 2008;103:113–512.
- [21] Maier K. *Phys Stat Sol* 1977;44:567.