



Effect of cooling rate after hot pressing on electrical conductivity of Si_3N_4 -ceramics with TiO_2 and TiH_2 additives

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Abstract

It has been established that cooling rate after hot pressing has influence on microstructure, electrical conductivity and charge storage in Si_3N_4 ceramics with TiO_2 and TiH_2 additives, which can be used as substrates for the large capacity microassemblies by Flip-Chip technology. It was shown that the critical cooling rate is $30^\circ\text{C}/\text{min}$ for the Si_3N_4 - TiO_2 and $50^\circ\text{C}/\text{min}$ for the Si_3N_4 - TiH_2 ceramics. Electrical conductivity is structurally sensitive property, strongly connected with evolution of Si_3N_4 microstructure. The best properties are typical for Si_3N_4 ceramics characterized by mono-trap state level with the activation energy of about 0.8 eV, obtained at the characteristic cooling rates.

Keywords: sialon, titanium oxide, titanium hydride, hot pressing, cooling rate, d.c. conductivity

I. Introduction

Designing of silicon nitride properties is still actual, but not enough investigated. It is known that properties of Si_3N_4 amorphous layers, synthesized in nonequilibrium conditions, are sensitive to different technology factors [1]. Thus, heating and cooling modes play the important role in formation of grain structure and composition of an insulating material. Heating mode determines chemism and kinetics of interaction between different components [2], but cooling rate after hot pressing governs the crystallization and amorphization processes.

Ideal activating additive for good consolidation of sialons during hot pressing should turn into a liquid phase at sintering temperatures [3]. It is reported [4] that addition of small amount of titanium compounds to precursor mixture for production of sialons reduces sintering temperature and increases temperature interval of existence of melt in grain boundary region. During in-

teraction of titanium with β - Si_3N_4 solid solutions can be formed [5]. Titanium compounds can be added to precursor mixture in the form of TiO_2 or TiH_2 . Application of TiO_2 prevents the abnormal grain growth during sintering of Si_3N_4 [6–8]. On the other hand, to improve fracture strength of silicon nitride ceramics compounds with high-melting point and high diffusion coefficient, for example TiH_2 , can be used [9]. Hydrogen also activates material consolidation. In addition, on the end of isothermal soaking during hot pressing the liquid phase can be depleted by aluminum and titanium ions. Thus, it is possible to obtain electroneutrality violation of crystallized grain-boundary phase, which is compensated by localization of hydrogen with formation of many weakly bounded defects.

There is still not enough information about: i) which technology factors has effect on sialon so that it comes to amplification or impairment of defect generation, ii) which type of trap levels arises in hot pressing sialon and iii) how traps participate in processes of an electromigration and polarization of ceramic composites. It is also important to develop additional appropriate methods for non-destructive quality control of Si_3N_4 ceramics.

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The objectives of this work are to investigate microstructure evolution and electrical conductivity of Si_3N_4 ceramics with TiO_2 and TiH_2 additives obtained by different cooling rate after hot pressing and to ascertain the interaction: technology - structure - properties.

II. Experimental

Silicon-nitride ceramics with TiO_2 (sample Si_3N_4 - TiO_2) and TiH_2 (sample Si_3N_4 - TiH_2) additives were prepared from β - Si_3N_4 powder, 92 vol% (Baku plant of powder metallurgy, Azerbaijan, with chemical composition given in Table 1) by hot pressing at 1700°C . A grain boundary phase was formed from: i) chemically pure α - Al_2O_3 powder, 5 vol% (Nikolaev aluminous plant, Ukraine), ii) titanium oxide, 3 vol% (Zaporozhye Titanium-Magnesium plant, Ukraine) or titanium hydride, 3 vol% (Donetsk chemical plant, Ukraine). Powder mixtures were prepared in planetary-type mill for 15 minutes in acetone with aluminum oxide balls. Pressing temperature was controlled by heat-radiation pyrometer OPIR-17 on wall of a graphite matrix through a hole in the screen with accuracy $\pm 10^\circ\text{C}$. Isothermal soaking has been made throughout 30 minutes under pressure of 20 MPa in air. Different cooling rate (V_c) of samples after hot pressing were used: 10, 20, 30, 40, 50, 60, 90 $^\circ\text{C}/\text{min}$. The obtained samples had size of $10\text{ mm} \times 10\text{ mm} \times 5\text{ mm}$.

XRD data were obtained by X-ray apparatus DRON-3. The amount of phases was determined by

the intensities ratio of certain analytical dashes of each phase (equation 1).

$$\frac{I_{HKL}^\alpha}{I_{H_1K_1L_1}^\beta} = K_{\alpha\beta} \frac{V_\alpha}{1-V_\alpha} \quad (1)$$

Interaction factor $K_{\alpha\beta}$ was determined experimentally by comparison of X-ray patterns of well-known pre-mixes. Relative volume of one of the phases was determined in accordance to equation 2.

$$V_\beta = 1 - V_\alpha \quad (2)$$

Images of materials' microstructure were obtained by microscope Neofot and the picture scanner Epikvant. The quantitative analysis of images was made with the analyzer SIAMS-620.

Electrical conductivity (direct current), at different temperatures up to 600°C , was measured by an electrometer with an input resistance of $10^{12}\ \Omega$ at a running voltage of 100 V. Samples were heated-cooled in the exterior furnace with the temperature rate of $4\pm 1^\circ\text{C}/\text{min}$ in a measuring chamber, providing fixed contact with a force of 10 kPa [10].

III. Results and discussion

3.1 Phase composition and microstructure

Characteristics and mechanical properties of the sintered Si_3N_4 - TiO_2 and Si_3N_4 - TiH_2 samples are given in Table 2. Porosity of all sintered samples is between 4

Table 1. Chemical composition and particularly impurities of starting powder β - Si_3N_4

Chemical composition of β - Si_3N_4 precursor powder												
Si_{gen}	N	$\text{Si}_{\text{uncomb}}$	Fe	Al	Ca	O	Mg	Ti	C_{gen}	C_{uncomb}	Mn	Ni
58.8	36.2	0.15	0.42	0.40	-	1.56	-	-	1.4	<0.1	<0.1	<0.1

Table 2. Characteristics of the sintered samples

Additive	Cooling rate [$^\circ\text{C}/\text{min}$]	Porosity [%]	K_{IC} [$\text{MN}/\text{m}^{3/2}$]	H_μ ($P = 5\text{ N}$) [GPa]
TiO_2	10	5.2	5.6	14.0
	20	5.7	6.5	16.1
	30	6.0	6.4	14.5
	40	5.2	5.8	16.9
	50	5.2	6.9	15.8
	60	4.4	6.5	16.7
	90	5.0	5.4	14.0
TiH_2	10	4.6	5.4	14.3
	20	5.0	6.7	14.7
	30	4.7	6.8	14.3
	40	4.0	6.3	13.9
	50	4.3	6.0	13.5
	60	4.0	6.1	13.0
	90	4.3	5.4	14.0

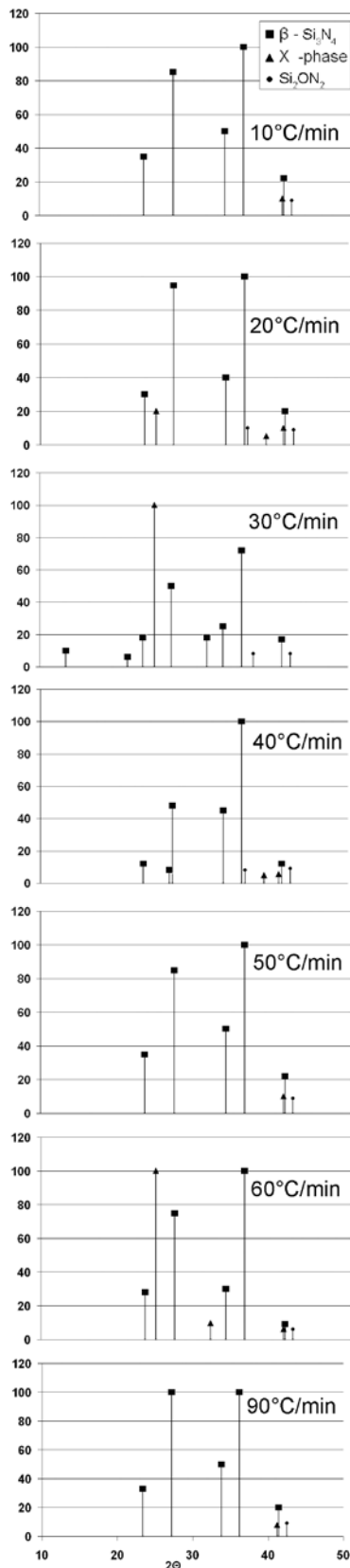


Figure 1. XRD results of Si_3N_4 ceramics with the TiO_2 additive prepared with different cooling rate presented by positions of characteristic peaks

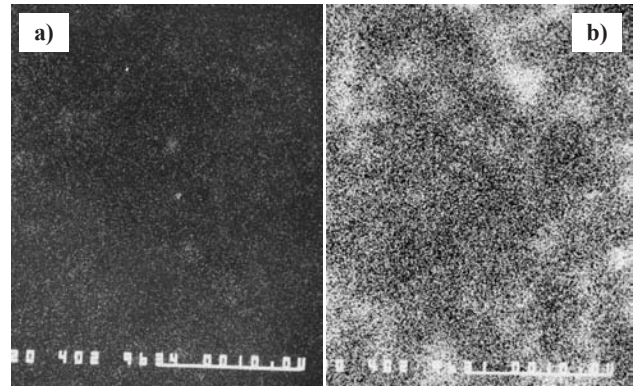
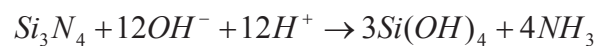
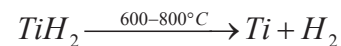


Figure 2. SEI (‘‘compo’’) of Si_3N_4 ceramics with the TiO_2 (a), TiH_2 (b) additives in characteristic oxygen radiation

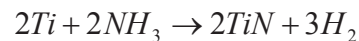
and 6 vol% and the corresponding density between 3.0 and 3.1 g/cm^3 . It can also be seen that the influence of cooling rate on mechanical properties is negligible.

XRD results (presented in Fig. 1 only by positions of the characteristic peaks) confirmed that beside the basic $\beta\text{-Si}_3\text{N}_4$ phase two additional phases, X_1 and Si_2ON_2 , were found in all sintered samples. These two secondary phases were formed during cooling of the liquid phase (obtained at the sintering temperature) around the solid $\beta\text{-Si}_3\text{N}_4$ grains. It can also be seen that the cooling rate after hot pressing has influence on phase composition, i.e. the state of these secondary phases (Fig. 1).

As can be seen from the Fig. 2, addition of titanium to silicon nitride ceramics in the form of TiH_2 (in comparison with TiO_2) considerably increases the oxygen content in system. Probably, this situation can be caused by titanium hydride dissociation at 600–800°C with the subsequent formation of hydroxyl complexes which hydrate silicon nitride [11].



Also, formation of titanium nitride complexes is possible.



In this case, increase of the oxygen content in $\text{Si}_3\text{N}_4\text{-TiH}_2$ ceramics is caused by $\beta\text{-Si}_3\text{N}_4$ -crystallites surface oxidation.

3.2 Electrical d.c. conductivity

Electrical d.c. conductivity (σ) of the sintered samples was measured in heating-cooling mode and some of the results (for the samples with cooling rate of 30 and 90°C/min) are presented in Figs. 3 and 4. Non-linear temperature dependence of d.c. conductivity can be observed and it is connected with release of weekly bounded carriers localised at attachment levels*. Only

*Attachment level is a level at which probability of electron ejection in conduction band is higher than probability of its recombination with the hole in valence band, and occurrence depth can be compared with kT (<0,4–0,5 eV). Electron is in delocalized state, and its wave function has continuous spectrum

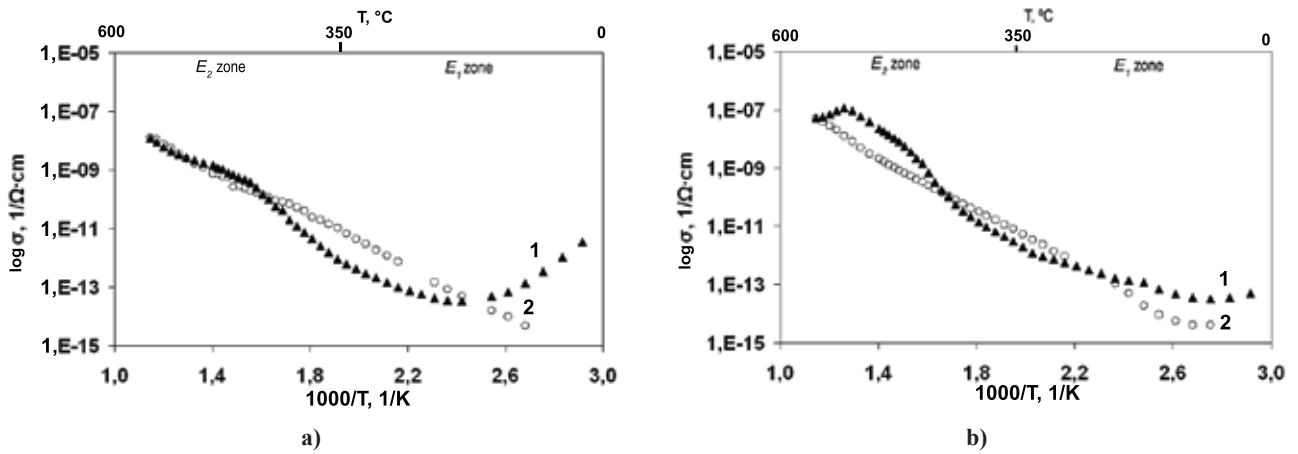


Figure 3. Temperature dependences of conductivity of samples with TiO_2 additives during heating (1) and cooling (2) with the rates $V_c = 30$ (a) and $90^\circ\text{C}/\text{min}$ (b)

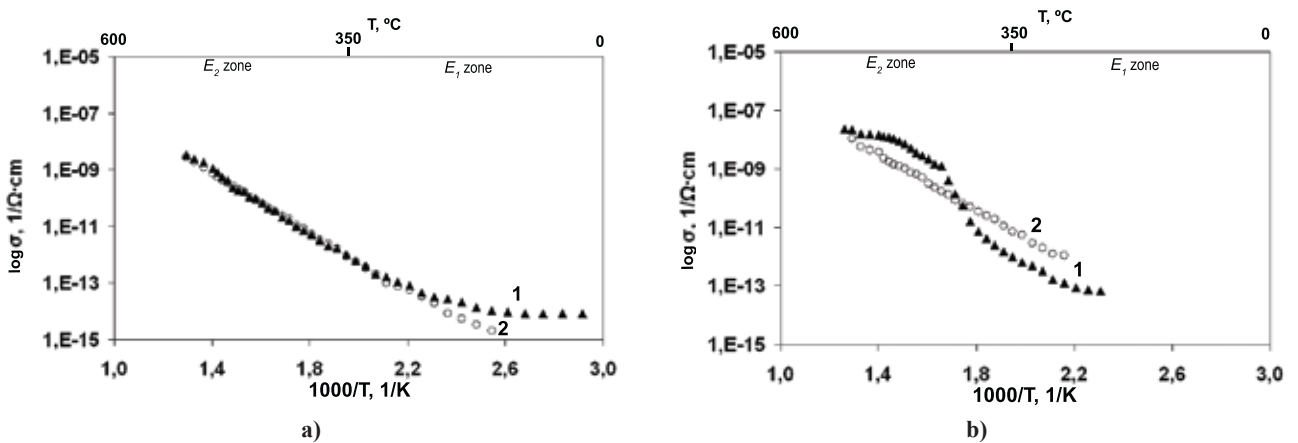


Figure 4. Temperature dependences of conductivity of samples with TiH_2 additives during heating (1) and cooling (2) with the rates $V_c = 30$ (a) and $90^\circ\text{C}/\text{min}$ (b)

decreasing dependence $\sigma(T)$ was analyzed as analysis of increasing dependence was obstructed by releasing of redundant carriers on capture levels. Temperature dependence of electrical conductivity follows the Arrhenius law with different activation energies, E_a (which describes the depth of carrier localization level) for various cooling rates of a composite after hot pressing. It is possible to distinguish two areas on temperature dependence with different E_a : i) area E_1 in low-temperature region $100\text{--}350^\circ\text{C}$ and ii) area E_2 in high-temperature region $350\text{--}600^\circ\text{C}$. Accordingly, activation energy for carriers in materials with different additives (TiO_2 and TiH_2) was calculated and presented in Figs. 5 and 6 in correlation with cooling rate after hot pressing (HP). Few characteristic zones of correlation can be seen.

If the electric field is applied along direction of HP (Fig. 5), it is possible to distinguish two characteristic regions separated by the critical cooling rate at which crystallization of structural components starts. They are $30^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$ for the $\text{Si}_3\text{N}_4\text{-TiO}_2$ and $\text{Si}_3\text{N}_4\text{-TiH}_2$ ceramics, respectively. If cooling rate exceeds critical one, for the material with TiH_2 additive, occurrence depth in both (low and high) temperature regions

is equal to 0.9 ± 0.05 eV and does not depend on technological cooling rate (Fig. 5a).

For the $\text{Si}_3\text{N}_4\text{-TiO}_2$ ceramics, different occurrence depths for low and high-temperature region are observed, 0.9 ± 0.05 eV and 1.2 ± 0.05 eV, respectively (Fig. 5b). On the other hand, the samples cooled by rate which is lower than the critical one (Fig. 5) behave differently.

There is one stable level for the material with TiH_2 additive, which is not dependent on technological cooling rate (1.2 ± 0.05 eV), and a spectrum of trap levels with activation energies 0.8 ± 0.05 eV and 0.4 eV (the minimum at $V_c = 30^\circ\text{C}/\text{min}$). For the $\text{Si}_3\text{N}_4\text{-TiO}_2$ ceramics (Fig. 5b) activation energy in low-temperature region decreases a little (from 1.3 to 0.8 eV), but in high-temperature region increases considerably (from 0.6 to 1.2 eV).

If the electric field is applied perpendicularly to direction of HP, activation energy of carriers for the material with TiH_2 additive (Fig. 6a) depends parabolically on technological cooling rate. For cooling rates between $30\text{--}60^\circ\text{C}/\text{min}$ two levels of carriers occurrence, at 1.2 ± 0.05 eV and 0.9 ± 0.05 eV, exist. At higher cooling rate energy level of 0.8 ± 0.05 eV was calculated for

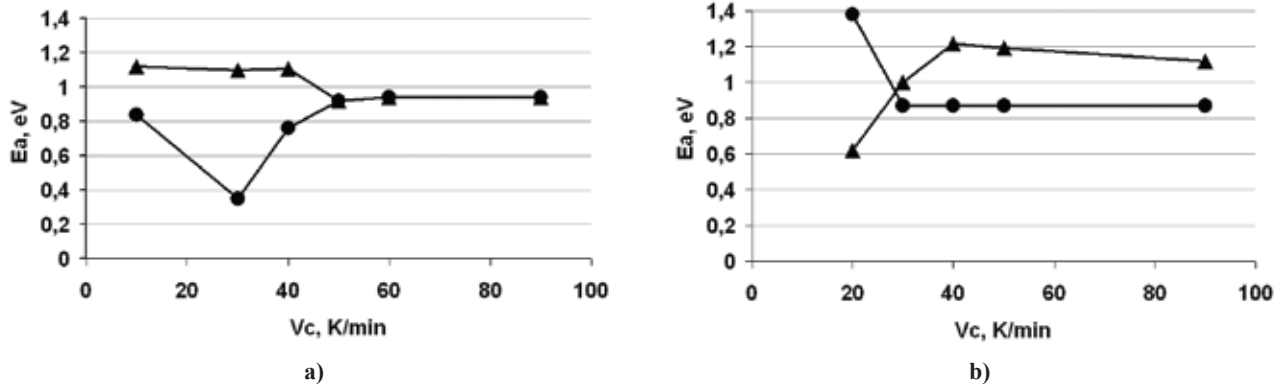


Figure 5. Activation energy distribution of low- E_1 (●) and high-temperature regions E_2 (▲) of electrical conductivity of Si_3N_4 ceramics with the TiH_2 (a) and TiO_2 additives (b) (electric field is parallel to direction of HP)

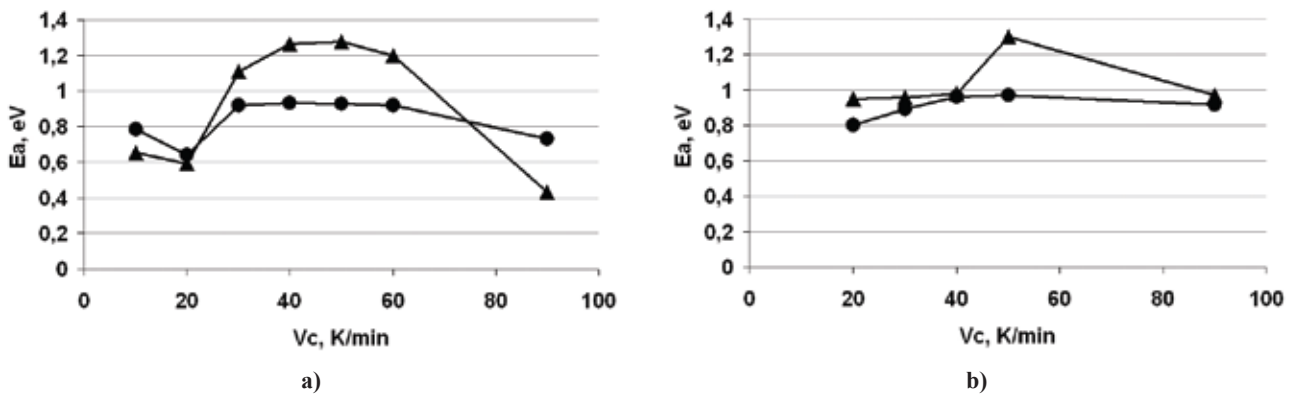


Figure 6. Activation energy distribution of low- E_1 (●) and high-temperature regions E_2 (▲) of electrical conductivity of Si_3N_4 ceramics with the TiH_2 (a) and TiO_2 additives (b) (electric field is perpendicular to direction of HP)

low-temperature region and remarkable reduction of activation energy (from 1.2 to 0.4 eV) for high-temperature region. In the Si_3N_4 ceramics with TiO_2 additives (Fig. 6b) structural components appear. There is a spectrum of energy levels with occurrence depth from 0.8 to 0.9 eV (“a tail of trap states”) in the forbidden zone of such structural components. Only by cooling rate close to the critical one ($V_c = 50^\circ\text{C}/\text{min}$) occurs a stable energy level of deep occurrence with $E_a = 1.2$ eV.

Silicon nitride Si_3N_4 is the compensated semiconductor, which contains both donor (at the expense of a doping with oxygen) and acceptor (at the expense of a doping with aluminum) levels in a forbidden zone. Thorp and Sharif [12,13] speak about conductivity of p-

type at temperatures lower than 500°C and n-type above 900°C . In the work [14] occurrence depth of trap levels is theoretically calculated for various types of defects (Table 3). It is shown that the values, calculated and obtained by us, correlate well with each other. It tells about structural sensitivity of electrical conductivity. We can assert that the technological mode, and namely the cooling rate of samples, influences morphology of structure and films formation on boundaries of crystalline grains of multicomponent materials, first of all on a crystallization degree of a grain boundary phases.

So by technological cooling rate which is higher than the critical one, the maximum contribution to electrical conductivity is made by the structural components with

Table 3. Results of calculation of trap electronic structure in amorphous film $\text{Si}_3\text{N}_4\text{-SiO}_2$

Level	Type of defect	Type of trap	Occurrence depth of level, [eV]	Comments
A	Two coordinated nitrogen atom in amorphous Si_3N_4	For electrons	0.8	For holes a defect is a trap only in oxygen-enriched silicon oxynitride
B	Silicon-silicon bond by formation of nitric vacancy in amorphous Si_3N_4	For electrons	1.6	
B'		For holes	1.0	
C	Two coordinated silicon atom (silicen centre) in amorphous SiO_2	For holes	1.5	Electron is not trapped with this defect

occurrence depth of about 0.8 eV, supposedly two coordinated nitrogen atoms in Si_3N_4 . Defect in the form of two coordinated atom of silicon in amorphous SiO_2 leads to formation of traps for holes with activation energy of about 1.2 eV. After transformation of silicon oxide to amorphous silicon as a result of dissociation, the occurrence depth of defective levels decreases from 1.2 to 0.8 eV. The same occurs, if the crystal grains Si_3N_4 with two coordinated atoms of nitrogen dominate in substance. The increase of occurrence depth of traps from 0.4 to 1.2 eV tells about defect origin in dehydrogenated films of amorphous silicon nitride, oxidation of these films and formation of defects in amorphous SiO_2 [15].

IV. Conclusions

Control of cooling rate after hot pressing of Si_3N_4 ceramics with TiO_2 and TiH_2 additives has influence on: crystallization and amorphicity, composition and state of grain boundary phase, and anisotropy of microstructure. It is shown that the critical cooling rate is $30^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$ for the $\text{Si}_3\text{N}_4\text{-TiO}_2$ and $\text{Si}_3\text{N}_4\text{-TiH}_2$ ceramics, respectively. It is also shown that cooling rate after hot pressing has influence on electrical conductivity and charge storage in Si_3N_4 ceramics. Electrical conductivity is structurally sensitive property, strongly connected to evolution of Si_3N_4 microstructure. The best properties are typical for Si_3N_4 ceramics characterized by monotrap level with occurrence depth of 0.8 ± 0.05 eV, obtained at the characteristic cooling rates.

References

1. A.V. Rjanov, *Silicium nitride in electronics*, Nauka, Novosibirsk 1982 (in Russian).
2. D. Sutor, G.S. Fishman, "Densification and sintering kinetics in sintered silicon nitride", *J. Am. Ceram. Soc.*, **75** [5] (1992) 1063–1067.
3. J.E. Wectin, "Crystallization of grain boundary phases in hot-pressed silicon nitride materials. Part 1. Preparation and characterization materials", *J. Mater. Sci.*, **13** (1978) 2137–2146.
4. V.J. Petrovskii, "Role of liquid phase in formation of properties of sialon ceramics", *CERAMICS*, **45** (1994) 41–50.
5. S. Hayashi, T. Hirai, R. Hiraga, "Microstructure of $\text{Si}_3\text{N}_4\text{-TiN}$ composites prepared by chemical-vapour deposition", *J. Mater. Sci.*, **17** (1982) 3336–3340.
6. J. Zhang, J.S. Yuan, Y. Ma, A.S. Oates "Design optimization of stacked layer dielectrics for minimum gate leakage currents", *Solid-State Electronics*, **44** (2000) 2165–2170.
7. C. Kawai, A. Yamakawa, "Crystal growth of silicon nitride whiskers through a VLS mechanism using $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ oxides as liquid", *Ceram. Int.*, **24** [2] (1998) 135–138.
8. R. Sabia, L. Ukrainczyk, "Surface chemistry of SiO_2 and $\text{TiO}_2\text{-SiO}_2$ glasses as determined by titration of soot particles", *J. Non-Cryst. Solids*, **277** [1] (2000) 1–9.
9. M.A. Kuzenkova, B.B. Ivzhenko, "Effect of additives of titanium hydride on the structure and strength of ceramics on the basis of silicon nitride", pp. 118 in *Methods of production, properties and application fields of nitrides – Zinatne, Riga*, 1984.
10. G.G. Gnesin, V.M. Kirilenko, V.Ya. Petrovsky "Quality control of hot pressed silicium nitride dielectric materials", *Powder Metal.*, **3** (1982) 53–59 (in Russian).
11. M.R. Freedman, J.D. Kiser, T.P. Herbell, "Factors influencing the ball milling of Si_3N_4 in water", *Ceram. Eng. Sci. Proc.*, **6** (1985) 1124–1134.
12. H.S. Thorp, R.I. Sharif, "Electrical conductivity in hot-pressed nitrogen ceramics", *J. Mater. Sci.*, **11** [8] (1976) 1494–1500.
13. H.S. Thorp, R.I. Sharif, "D.C. electrical properties of hot-pressed nitrogen ceramics", *J. Mater. Sci.*, **13** [2] (1978) 441–449.
14. V.A. Gritsenko, Yu.N. Novikov, A.V. Shapochnikov, Yu.N. Morokov, "Computational modeling of intrinsic defects in SiO_2 and Si_3N_4 ", *Phys. Techniq. Semiconduc.*, **35** [9] (2001) 1041–1049 (in Russian).
15. O.A. Golikova, M.M. Kazanin, "Hydrogenated amorphous silicon films with advanced photosensitivity", *Phys. Techniq. Semiconduc.*, **33** [1] (1999) 110–113 (in Russian).