PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

PROCESSOS DE DEGRADAÇÃO NO SISTEMA Al-TI-SI SOB CHOQUE TÉRMICO

DEGRADATION PROCESSES IN THE Al-TI-SI SYSTEM UNDER THERMAL SHOCK

ДЕГРАДАЦИОННЫЕ ПРОЦЕССЫ В СИСТЕМЕ Al-TI-SI В УСЛОВИЯХ ТЕРМОУДАРА

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Received 28 October 2019; received in revised form 22 January 2020; accepted 12 March 2020

RESUMO

Nos últimos anos, muita atenção dos desenvolvedores de microcircuitos integrados tem sido dada ao desenho de novos tipos de microprocessadores, desenvolvimento e masterização de circuitos tridimensionais multicamadas e criação de dispositivos baseados em semicondutores complexos. O objetivo do presente trabalho é estudar processos térmicos no sistema Al-Ti-Si multicamada até o desenvolvimento de processos de degradação. São considerados os problemas de degradação durante a metalização do alumínio com a deposição de uma subcamada de titânio na superfície de silício. É analisada a evolução dos processos de destruição irreversível do condutor de filme durante a passagem dos pulsos de corrente retangulares com energia de até 300 mJ e duração de 50 ... 1000 μs. Verificou-se que, sob a influência de um único pulso de corrente retangular com duração não superior a 80 μs e energia de 85 mJ, o derretimento de um filme de metal é um processo prioritário de destruição da estrutura. O aumento na duração do pulso (τ> 80 μs) altera a prioridade da degradação térmica, e o derretimento de contato se torna o principal mecanismo de destruição estrutural. Também foi descoberto que o recozimento isotérmico leva à melhoria nas propriedades condutoras de calor do sistema e ao aumento nas densidades críticas de corrente. Isso está associado a uma melhoria nas propriedades adesivas da estrutura, bem como a transformações de fase no sistema Al-Ti-Si durante o recozimento. Os resultados do artigo podem ser utilizados em estudos adicionais das propriedades do sistema AI-TI-SI, bem como na criação de estruturas semicondutoras, levando em consideração propriedades como alta condutividade elétrica, boa processabilidade, ausência de componentes químicos no sistema Al-Si, estabilidade química e tendência à eletromigração, a possibilidade de curto-circuito, alta mobilidade de difusão, baixo ponto de fusão, a incapacidade de conectar o fio por soldagem.

Palavras-chave: *microprocessadores, circuitos integrados tridimensionais, estruturas semicondutoras.*

ABSTRACT

In recent years, much attention of developers of integrated microcircuits is given to designing novel types of microprocessors, development, and mastery of technologies of both multilayer 3D integrated circuits and making devices based on complex semiconductors. The aim of the present work is to study thermal processes in the Al-Ti-Si multilayer system up to the development of degradation processes. The degradation issues in aluminum metallization with titanium sublayer deposited onto silicon surface are considered. The evolution of processes of irreversible destruction of film conductor under passage through it of single square-wave current pulses with energy up to 300 mJ and duration of 50…1000 μs was analyzed. It was found that, under the action of a single square-wave current pulse with a duration of no more than 80 μs and energy of 85 mJ, the priority process of structural damage is the melting of the metal film. Increasing pulse duration (τ > 80 μs) changes the priority of thermal degradation, and contact melting becomes the main mechanism of structure damage. It was also found that isothermal annealing leads to improving system heat-conducting properties and increasing critical current densities. This is related to the improvement of adhesion properties of the structure as well as with phase transformations in the Al-Ti-Si system in the course of annealing. The results of the article can be used in further studies of the properties of the AI-TI-SI system, as well as in the creation of semiconductor structures taking into

DOI: 10.52571/PTQ.v17.n34.2020.352_P34_pgs_335_342.pdf

account properties such as high electrical conductivity, good processability, the absence of chemical components in the Al-Si system, chemical stability, and a tendency to electromigration, the possibility of short circuit, high diffusion mobility, low melting point, the inability to attach the wire by soldering.

Keywords: *microprocessors, 3D integrated circuits, semiconductor structures*.

АННОТАЦИЯ

В последние годы большое внимание разработчиков интегральных микросхем уделяется проектированию новых типов микропроцессоров, разработке и освоению многослойных трехмерных интегральных схем, созданию устройств на основе сложных полупроводников. Целью данной работы является изучение тепловых процессов в многослойной системе Al-Ti-Si вплоть до развития процессов деградации. Рассмотрены вопросы деградации при металлизации алюминия с нанесением на поверхность кремния подслоя титана. Проанализирована эволюция процессов необратимого разрушения пленочного проводника при прохождении через него одиночных прямоугольных импульсов тока с энергией до 300 мДж и длительностью 50… 1000 мкс. Было установлено, что при воздействии одиночного прямоугольного импульса тока длительностью не более 80 мкс и энергией 85 мДж приоритетным процессом разрушения структуры является плавление металлической пленки. Увеличение длительности импульса (т> 80 мкс) меняет приоритет термической деградации, и контактное плавление становится основным механизмом разрушения конструкции. Также было обнаружено, что изотермический отжиг приводит к улучшению теплопроводящих свойств системы и увеличению критических плотностей тока. Это связано с улучшением адгезионных свойств структуры, а также с фазовыми превращениями в системе Al-Ti-Si в процессе отжига. Результаты статьи могут быть использованы при дальнейших исследованиях свойств системы AI-TI-SI, а также при создании полупроводниковых структур с учетом таких свойств, как высокая электропроводность, хорошая технологичность, отсутствие химических компонентов в системе Al-Si, химическая стабильность и склонность к электромиграции, возможность короткого замыкания, высокая диффузионная подвижность, низкая температура плавления, невозможность прикрепить проволоку пайкой.

Ключевые слова: *микропроцессоры, трехмерные интегральные схемы, полупроводниковые структуры.*

1. INTRODUCTION

In recent years, much attention of developers of integrated microcircuits is given to designing novel types of microprocessors, development, and mastery of technologies of both multilayer 3D integrated circuits and making devices based on complex semiconductors (Topol *et al.,* 2006). Mastery of new semiconductor devices and structures cannot be made without solving the problems of metallization and contact systems (Pedersen *et al.,* 2015). The point is that the role of metallization in modern structures of micro- and nanoelectronics is becoming a key (Chang and Chang, 2010; Okabe *et al.,* 2014; Brincker *et al*., 2018a; Brincker *et al.,* 2018b; Zhao *et al.,* 2019).

It is known that the performance of logic elements increases with downsizing, while those of interconnections and contacts decrease because of the reduction of the cross-section of film conductors and the growth of their linear resistance and electric capacity. As a result, starting from a certain integration level of semiconductor devices, signal delays in the interconnections may exceed those in the structures themselves. In addition, as the semiconductor cross-sections decrease, the problems appear that are related to electromigration in thin metal films and contact ohmicity (Kang *et al.,* 2008; Martineau *et al.,* 2014; Macherzyński *et al.,* 2016; De Rose *et al.,* 2018; Homa and Sobczak, 2019; Eslami *et al.,* 2019; Fischer *et al.,* 2019; Chawla *et al.*, 2019; Cruz *et al.*, 2019; Yi *et al.*, 2019). And technological complexities when making modern metallization systems (including the structures involving p-n junctions with small occurrence depth) should also be noted (Garosshen *et al.,* 1985; Macherzyński *et al.,* 2016).

Aluminum films are widely used as material for interconnections and ohmic contacts to silicon when making semiconductor structures (Garosshen *et al.,* 1985). This material has a number of advantages: high electrical conduction, good manufacturability, absence of chemical components in the Al–Si system, chemical stability of aluminum in oxidizing medium, etc. (Ahmad *et al.,* 2019; Kumar *et al.*, 2019; Kumar and Singh, 2019; Sattar *et al.*, 2019; Shuai *et al.*, 2019; Wang *et al.*, 2019b).

However, along with the above

advantages, aluminum metallization has a number of substantial disadvantages. The most important of them are as follows: tendency to electromigration, possibility of short circuit through dielectric in layered metallization systems (because of formation of spurs on a film due to electromigration and Al recrystallization), high diffusion mobility of A1 over the grain boundaries, low melting point (577°C) of the eutectic of Al-Si system, low mechanical strength of Al films, impossibility of wire attachment using soldering, etc. (Gupta, 1979; Ahmad *et al.,* 2019). Because of the listed disadvantages, multilayer systems with metal sublayers (including Al) are applied in ICs and transistors with shallow p-n junctions to get the basic current-carrying layer. In this case, usually, the first metal layer (sublayer) has high adhesion to both silicon and silicon dioxide and simultaneously has small solubility and diffusion coefficients in these materials. Titanium meets these requirements. For example, the use of ohmic contacts with titanium sublayer in fast-operating ICs made it possible to increase mean time between failures by a factor of 20 as compared to the Al-Si binary system (Brincker *et al.,* 2015). So the aim of the present work is an investigation of thermal processes in an Al-Ti-Si multilayer system up to the development of degradation processes.

2. MATERIALS AND METHODS

To perform experiments, the structures of the metal-sublayer-semiconductor plate type were formed. Aluminum was the main current-carrying layer because it is the most extended material used for metallization layers in semiconductor structures (Diligenti *et al.,* 1989). Molybdenum, titanium, and nickel were used for metal sublayers that improve the contact, adhesion and barrier properties of current-carrying systems (Macherzyński *et al.,* 2016; Ahmadvand *et al.*, 2019; Alam *et al.*, 2019; Galetz *et al.*, 2019; Liu *et al.*, 2019; Neudeck *et al.*, 2019; Sun *et al.*, 2019; Wang *et al.*, 2019a). Silicon plates doped with phosphorus and oriented along (Mwema *et al.,* 2018) direction, with resistivity ρ = 0.01 Ω·cm and 60 μm n-epitaxial layer (15 Ω·cm), served as substrates. Such substrates prevent shunting of metallization layers. Dielectric layers of silicon oxide or silicon nitride were grown preliminary on some substrates.

The deposition of films onto the pre-prepared surface of silicon plates was made by electron-beam evaporation in a single technological cycle (Macherzyński *et al.,* 2016; Mwema *et al.,* 2018). The substrate temperature (T = 373 K) and working pressure ($p = 7{\cdot}10^{-4}$ Pa) were maintained constant in the course of film deposition. They were controlled with a preliminary calibrated platinum–platinum-rhodium (Pt-PtRh) thermocouple (near the sprayed plates) and a vacuum gage. The aluminum (titanium) evaporation rates were V_1 = 2 nm/s (V_2 = 1.5 nm/s). (Hereinafter subscript "1" relates to Al, "2" relates to Ti interlayer and "3" relates to the semiconductor substrate.) Thickness h_1 of Al film was no less than 2 μm; thickness h_2 of metal sublayer varied in the 80…2000 nm range. Then the test structures described in (Skvortsov *et al.,* 2014; Skvortsov *et al.,* 2016) were made on the prepared multilayer structures using optical photolithography. Investigation of Al-Ti-Si multilayer systems before and after isothermal annealing was made for the obtained test structures (Skvortsov *et al.,* 2014; Skvortsov *et al.,* 2016) from electrical response taken from different their areas at the passage of single square-wave current pulses.

The temperature $T_1(t)$ of the metallization track was calculated from switching oscillograms $U(t)$ taken from an area of the test structure in the course of current pulse passage using Equation (1). Here R_0 = 0.88 Ω is the resistance of metallization track at T_0 = 290 K measured by the voltmeter-ammeter method; the area length ℓ = 2.9 mm; Al film thickness h_1 = 2.1 μm; track width b = 75 μm; $\alpha = 0.0043$ K^{-1} is the Al temperature coefficient of resistance. The typical experimental curves at passing a sequence of sinusoidal pulses are given in Figure 1. The obtained curves are also described by Equation (2) (Skvortsov *et al.,* 2014). They touch a range of temperatures preceding the beginning of degradation processes related to a thermal overload of the metallization system. Here λ is thermal conductivity; c, d and a are thermal capacity, density and thermal conductivity, respectively. It is evident that parameters related to the thermophysical properties of a thin-film system and silicon matrix depend on temperature. As before (Skvortsov *et al.,* 2016), their mean integral values were used to calculate T_1. The mean integral value of b is (Equation 3).

It is easy to verify from Equation (2) that dynamics of structure heating depend on current strength, parameters of semiconductor matrix and size-thermal ratio $(h_2/\bar{\lambda}_2)$ of a titanium film and intermediate dielectric film. So that the bigger is sublayer thickness, the quicker is heating of metallization tracks.

3. RESULTS AND DISCUSSION:

The results of experiments (Figure 1) fully confirm that as thickness h_2 of titanium sublayer changes from 80 nm to 170 nm, the temperature T_1 of Al film increases from 360 K to 430 K to the moment of pulse shutdown ($t = 500$ μs). This indicates a higher thermal load of multilayer structures as compared with the Al-Si binary system. Moreover, the estimation of values of titanium film thermal conductivity from Equation (2) and experiments (Figure 1) are overvalued. This indicates the necessity of stabilization annealing to improve adhesion and phase transformations in the Al-Ti-Si system. Indeed, preliminary stabilizing annealing at 500 °C in protective nitrogen atmosphere improved parameters of heat transfer of multilayer structures. This reflected in switching oscillograms (Figure 2). The observed improvement of heat sink processes also reflected on the development of thermal degradation of the structure (Dunn *et al.,* 1986; Skvortsov *et al.,* 2016; He *et al.,* 2019).

Earlier it was found out (Skvortsov *et al.,* 2014) that beginning of degradation processes in the studied range of current densities $j = (2\text{-}9)\cdot 10^{10}$ A/m^2 and pulse durations $\tau = (100\text{-}1000)$ μs is related to formation of molten zones in a thin-film system and subsequent melting of the total current-carrying layer (at the appropriate power of current pulses). The beginning of thermal damage is attributed to the moment of the abrupt departure of potential $U(t)$ from a monotonic increase in the switching oscillogram (Figure 3). The current density and starting point of irreversible changes in the structure will be called critical j_{cr} and t_{cr}, respectively. As already noted, isothermal annealing of thin-film structures (contributing to the improvement of thermal contact between the layers) has to lead to increasing critical current density j_{cr} at a fixed pulse duration τ. Indeed, the data obtained for the Al-Ti-Si structures confirm this (Figure 4). For single square-wave pulses with a duration of 200 μs and 550 μs, j_{cr} value may increase to 20%.

The observed changes are related to both improvement of adhesion in multilayer structure and active mass transfer (Chen, 2005), with the formation of triple chemical compounds based on titanium disilicide ($TiSi_2$) and replacement of titanium atoms with silicon atoms and (or) aluminum atoms ($Ti_xSi_yAl_z$). Such atomic rearrangement occurs with the participation of processes of grain boundary diffusion and bulk diffusion and is accompanied by the formation of new phases. All this significantly affects the electrical and thermal characteristics of the formed multilayer structure and reflects on switching oscillograms and j_{cr} value. As to the character of structure melting after the passage of the current pulse, the melting of aluminum tracks on the Al-Ti-Si system was characterized by regular directivity (Figure 5). Such behavior is related to good adhesion of titanium film to both contacting phases (Al and Si), even without stabilizing annealing. Annealing of the Al-Ti-Si structures did not change melting character; only structure electrical and thermal characteristics varied.

4. CONCLUSIONS:

The article examined the contribution of scientists to the study of the role of metallization in the structures of micro- and nanoelectronics, the operating characteristics of logic elements in various conditions. A characteristic of the use of aluminum in electronics, its positive properties and disadvantages was given. Degradation processes in the Ai-Ti-Si system were considered under thermal shock. Heating of a multilayer system at passing through it single square-wave current pulses with a duration of 50…1000 μs and amplitude j to $9\cdot 10^{10}$ A/m^2 was analyzed.

For the obtained test structures, a study was performed of Al-Ti-Si multilayer systems before and after isothermal annealing according to the electric response taken from different regions during the passage of one square. It was found that the dynamics of heating the structure depends on the current strength, the parameters of the semiconductor matrix and the size-thermal ratio of the titanium film and the intermediate dielectric film. Accordingly, the bigger the sublayer thickness is, the quicker the heating of metal tracks occurs: when the thickness h_2 of the titanium sublayer changes from 80 nm to 170 nm, the temperature T_1 of the Al film increases from 360 K to 430 K to the moment of pulse shutdown.

It was revealed that isothermal annealing leads to the improvement of heat-conducting properties of the system and, consequently, to increase critical current densities by 20%. This was related to the improvement of adhesive properties of the structure as well as to phase transformations in the Al-Ti-Si system in the course of annealing (atomic rearrangement took place with the participation of grain boundary diffusion and bulk diffusion processes), which affected the electrical and thermal characteristics of the formed multilayer structure and was reflected in the switching of the oscillograms. The melting of aluminum tracks in the Al-Ti-Si system was characterized by a regular directivity, which was associated with good adhesion of the titanium film to both contacting phases. It was observed that only the structure of electrical and thermal characteristics changed, but the nature of melting did not change.

5. ACKNOWLEDGMENTS:

The reported study was funded by RFBR, according to the research project No. 18-29-27005.

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$$U(t) = I(t)R_0\{1 + \alpha[T(t) - T_0]\}. \qquad \text{(Eq. 1)}$$

$$\Delta T = T_1 - T_0 = \frac{I^2 \bar{R}_1}{S}\left(\frac{h_2}{\bar{\lambda}_2} + \frac{1}{\bar{c}_3 \bar{d}_3}\sqrt{\frac{\tau}{\bar{a}}}\right) \qquad \text{(Eq. 2)}$$

$$\bar{b} = \frac{1}{\Delta T}\int_{T_0}^{T_1} b(T)\,dT \qquad \text{(Eq. 3)}$$

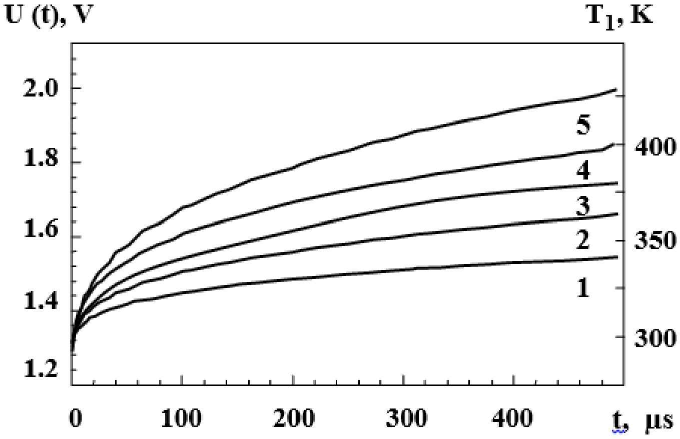

Figure 1. Switching oscillograms of Si-Ti-Al system at different Ti sublayer thicknesses: 1 – h_2=0; 2 – h_2=80; 3 – h_2=100; 4 – h_2=130; 5 – h_2=170 nm; j=6.0·10^{10} A/m^2; h_1=2 µm; pulse duration of 500 µs

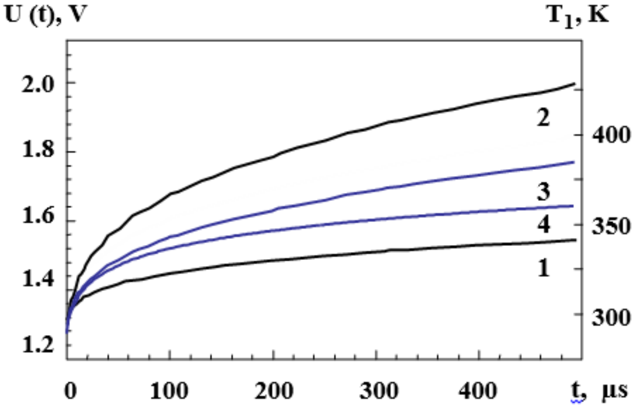

***Figure 2.** Switching oscillograms of Al-Si (1) and Al-Ti-Si systems with Ti sublayer thickness h_2=170 nm (2) after isothermal annealing of the structure at 500℃ for 3 – 60 min.; 4 – 90 min*

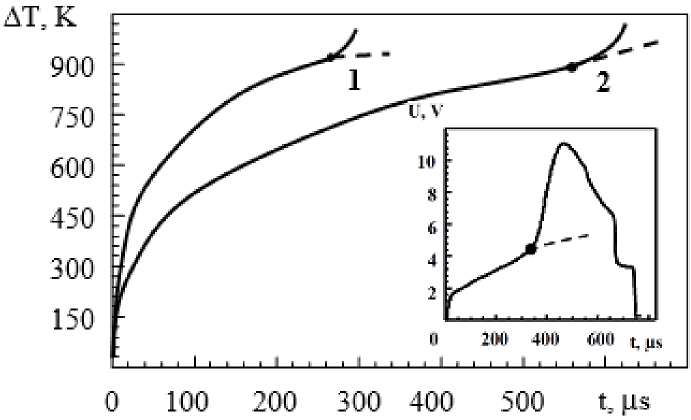

***Figure 3.** Dynamics of the temperature of aluminum metallization $\Delta T_1(t)=T_1(t)-T_0$ at the passage of a single current pulse with amplitude: 1 – j=8.7·10^{10} A/m^2; 2 – 7.0·10^{10} A/m^2. Insert: switching oscillogram of Si-Ti-Al systems taken at the passage of a single current pulse (duration of 800 µs, the amplitude of 6.4·10^{10} A/m^2)*

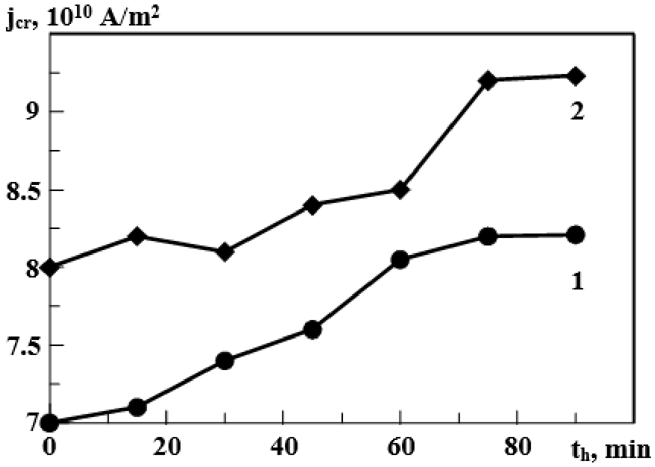

Figure 4. *Dependence of critical current density j_{cr} on annealing time t_h of Al-Ti-Si structure in an inert atmosphere at a temperature of 500°C; duration of square-wave current pulse: 1 – 550 μs; 2 – 200 μs*

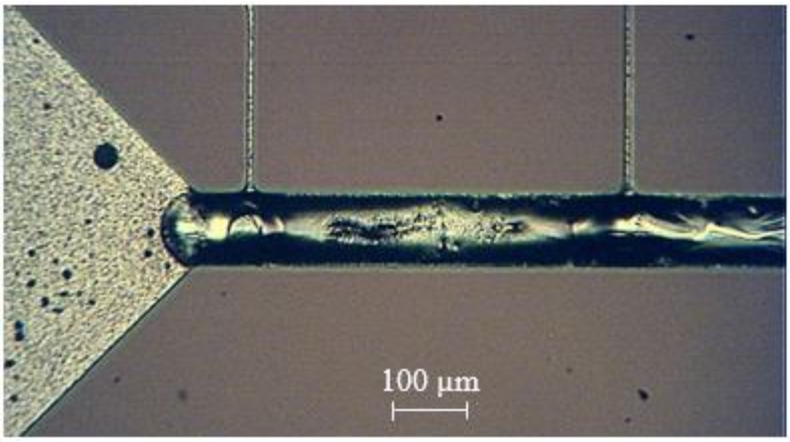

Figure 5. *Photograph of thermal degradation of Al-Ti-Si structure after current pulse passage ($j>j_{cr}$)*