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Thermoelastic interactions in Al–n–Si–Ni structures at pulse laser irradiation

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Using the scanning electron microscopy and optical metallography, the formation and redistribution of structural defects in the near-contact silicon layer of thermally untreated Al–n–Si structures resulting from thermoelastic stresses developed under pulse laser irradiation have been investigated experimentally. A structurized transition layer has been found to be formed at the metal/semiconductor interface at relaxation of elastic stresses in the metal layer. To explain the behavior features of the defect systems at the periphery of Schottky diodes under irradiation of Al–n–Si structures through a silicon optical window, a physical model of the laser radiation effect on the metal/semiconductor contact has been proposed taking into account temperature dependence of the radiation absorption coefficient in the semiconductor.

Методами растровой электронной микроскопии и оптической металлографии экспериментально исследовано процессы формирования и перераспределения структурных дефектов в приконтактном слое кремния термически неотожженных структур Al–n–Si вследствие проявления термоупругих напряжений при импульсном лазерном облучении. Обнаружено формирование структурированного переходного слоя на границе металл-полупроводник при релаксации упругих напряжений в металлизации. Для объяснения особенностей поведения систем дефектов по периметру диодов Шоттки при облучении структур Al–n–Si через кремниевое оптическое окно предложена физическая модель воздействия лазерного излучения на контакт металл-полупроводник, учитывающая температурную зависимость коэффициента поглощения излучения в полупроводнике.

The physical mechanism of the laser correction and parameters stabilization of current-voltage characteristic of Al–n–Si diodes with a Schottky barrier (SD) is possible to explain by density decrease of the deep levels bound with structural impurity defects in a space charge region (SCR) of a semiconductor due to relaxation of thermoelastic stresses in the structure layers after a pulse laser irradiation (PLI) [1–4]. However, the real metal/semiconductor contacts (MES) have a complex structure in which the thickness of transition layer between metal and semiconductor formed as a result of previous heat treatment before PLI can be comparable to the metal thickness. Therefore, thermoelastic stresses in the silicon SCR originating under PLI of vertical thin-film Al–n–Si structures may be distorted considerably by transition layer. A more essential development of elastic interaction processes in MES is expected to be observable at PLI of Al–n–Si close contacts not exposed to previous heat treatment obtained by aluminum evaporation onto a silicon surface cleaved in vacuo. As the evacuated chamber is unsealed after the ion-cleaning process, a natural SiO_2 oxide layer of 10 to 15 Å depth is formed on the silicon surface prior to the metal sputtering. If the cleaning is carried out by chemical liquid-phase etching, the oxide layer may achieve several hundreds of Angstrom units, that, naturally, deteriorates the aluminum film adhesion. The latter fact might probably explain the Al scaling at $d_0 > 1500$ Å thickness under PLI in experiments described in [4]. The purpose of this work was to simulate experimentally the of thermoelastic interaction processes in near-contact aluminum

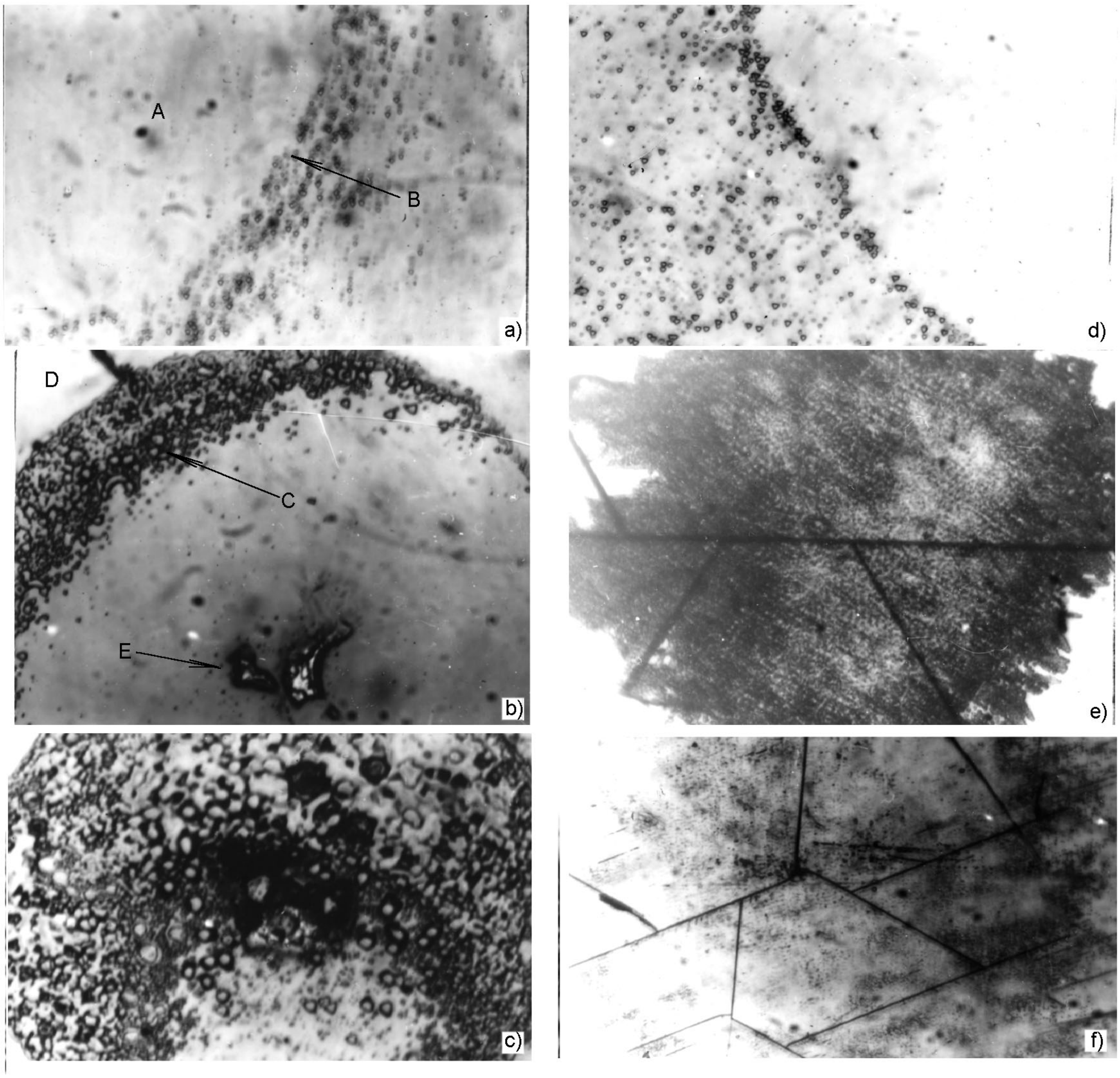

Fig. 1. Optic images of silicon surface after PLI and aluminum etching in Al–n–Si–Ni Schottky diodes irradiated from the aluminum contact side (a–c) and through silion substrate (d). Center of the silicon surface irradiated at $I_0 \approx 115$ (e) and 125 W/cm^2 (f). MIM-7 microscope, ×350.

and silicon layers of Al–n–Si–Ni SD not exposed to the preliminary heat treatment. Such layers are described with a physical model of a MES with a tunnel-shallow layer of a dielectric at a metal/semiconductor interface.

Two groups of Al–n–Si–Ni contacts were used in experiments. The structures were prepared on industrial chips of KEF-1 (111) silicon using one and the same technological route. By chemical etching, SiO_2 was removed from the whole working surface of a plate and the latter was cleaned by reactive ion etching (RIE). The Si layer removed by RIE was about 0.1 μm thick. After washing of silicon plates in $HF{:}H_2O$, aluminum was evaporated onto the working surface at the thickness $h = 0.6$ μm, and photoengraving on aluminum was carried out. The first group of structures was irradiated by a laser from the side of aluminum contact, while the second one, from the side of the silicon non-working surface. The ohmic contact was obtained by chemical nickel plating of the non-working surface of Al–n–Si structures after PLI. The structures under study were not expose to thermal annealing. The conditions of the pulse laser irradiation corresponded to [1]: wavelength $\lambda = 1.06$ μm, pulse duration $\tau = (1\div4)\cdot10^{-3}$ s, intensity $I_0 = (20\div170)\cdot10^3$ W/cm^2.

After layer-by-layer chemical etching of the structures, the surface morphology of various aluminum and silicon layers was examined by optical microscopy and microstructure of defects, by scanning electron

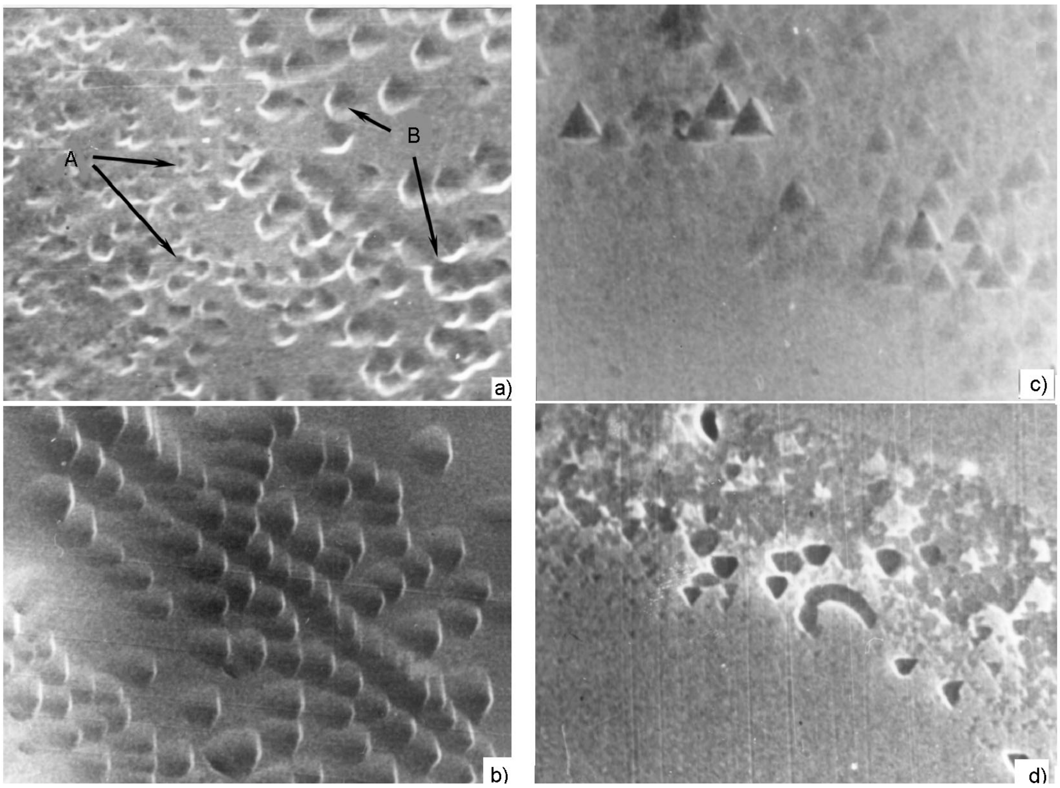

Fig. 2. Surface morphology of satellite plates (a, b) and Al–n–Si–Ni Schottky diodes (c, d) after PLI and aluminum etching. (a) I_0 = 115 W/cm^2 (A, etch pits near to the irradiation spot center; B, those at the periphery thereof); (b) I_0 = 125 W/cm^2; (c) $I_0 < I_c$; etch pits outside the aluminum contact; (d) $I_0 > I_c$; etch pits under the aluminum contact. Scanning electron microscope, ×1500.

microscopy in the of secondary electron mode [2, 3]. To improve the detection accuracy of the structural impurity defects, the plates were dressed with water solution containing palladium chloride hydrate $PdCl_2:2H_2O$, hydrofluoric acid and $K_3[Fe(CN)_6]$.

The metallographic examination of the first group of contacts at various PLI intensity I_0 has shown that the intensity critical value I_c in excess of which the morphological changes of the irradiated Al surface are observed exceeds similar values for thermally annealed Al–Si MES [1, 3] by 10–20 kW/cm^2 and attains 105–115 kW/cm^2.

The redistribution of the packing defects typical of Si (111) orientation, in subsurface silicon layer in the region of aluminum contact and outside thereof is shown in Fig. 1. As the radiation intensity increases from 80 kW/cm^2 up to 105 kW/cm^2, the surface defect density in Si under aluminum contact (Fig. 1a, site A) is reduced while a considerable increase in that density outside MES (Fig. 1a, site B) is observed. The PLI of the intensity $I_0 > I_c$ induces a reverse effect, namely, a defect cluster inside the contact (Fig. 1b, site C) at their complete absence outside MES (Fig. 1b, site D). The increase of I_0 up to 125 kW/cm^2 is accompanied by formation of a continuous porous defect layer at the Al–Si interface under the Al film (Fig. 1c). It is to note that, as well as under the corresponding PLI conditions of thermally annealed Al–Si structures [1], the phase interaction between Al and Si in the contact field occurs in the solid phase. In the site of an increased absorption of the radiation energy (Fig. 1b, site E), a local melting of the structure is possible.

No changes in the Al surface morphology are observed at an irradiation of a MES through the silicon substrate. However, at $I_0 > I_c$, defect clusters and exits of a grid of dislocation lines are well seen on the irradiated silicon surface after chemical etching. At $I_0 >$ 115–120 kW/cm^2, an amorphization of the silicon surface (Fig. 1e) or development of microcracks on cleavage planes according to the chip crystallographic orientation (Fig. 1f) take place. For Si (111), angles between directions of microcracks make 60 or 120°. Formation of photoinduced defects similar to those described in [2] was not observed at PLI conditions used in our experiment.

The effect of defect system redistribution at the working surface of silicon as a result of thermoelastic stresses in the second group MES is expressed less clearly and is characterized by some specific features. At $I_0 \approx I_c$, a separate chain of defects as adjoining equilateral triangular pits is formed at the periphery of aluminum contact. An insignificant increase in I_0 results in increase of the surface defect density outside the SD and propagation of the defect layer from MES by a distance ranging from 3–5 μm to 20–70 μm (Fig. 1d). A greater increase of $I_0 > I_c$, as well as that of irradiation intensity at $I_0 < I_c$, results in disappearance the above effect. At fixed intensity I_0, an extension of the MES diameter from 100 up to 800 μm is accompanied by an increasing surface defect density outside MES (approximately by one decimal order) and an extension of the defect propagation outside the contact. This confirms the model of thermoelastic phase interaction at Al–Si interface. The defect layer in silicon determined from the linear dimensions of etch pits makes $l \approx$ 3–5 μm at I_0 = 95–110 kW/cm^2.

Microstructure of separate defects and features of the defects system formation on the silicon surface under irradiation of a continuous film aluminum on satellite plates is shown in Fig. 2. It is characteristic that at $I_0 <$ 110 kW/cm^2, the defect size at the center of the irradiation spot (Fig. 2a, site A) in 2–4 times smaller than that at the spot periphery (Fig. 2a, site B) and the defects are distributed chaotically. The defects stimulated by an exit of dislocation lines located under certain angles to the working surface and oriented in various manners in the chip bulk. This may be due both to relaxation of existing defects caused by thermoelastic stresses attainable in the irradiation spot center at $I_0 \approx I_c$ and to formation of new defects outside the center. The total picture is defined by values of elastic stresses which arise at characteristic distances at the PLI of a MES by single pulses. The I_0 increase up to 125–130 kW/cm^2 favors the formation and ordering of a dislocation grid according to basic crystallographic directions of the silicon plate (Fig. 2b).

At the SD periphery, it is just the dot defects and their aggregations that predominate. Those are observed as equilateral pits both outside MES (Fig. 2c) at $I_0 < I_c$, and inside SD at $I_0 > I_c$ (Fig. 2d). This fact can be explained by development of plastic strains in the subsurface silicon layer. In the first case, the mechanical stresses do not exceed the elasticity limit of the metal film while in the second one, those result in fracture of the aluminum film in MES. Since the elastic stresses are directly proportional to increase in the material linear dimensions, at I_0 a little bit exceeding I_c, the failure of aluminum contact begins at the MES periphery where the elastic stresses are higher than at the center due to large strains. An increased Al diffusivity in Si is to be expected in this case, since under PLI, elastic tensile stresses appear in Si contact layer and compression ones in Al contact area (Fig. 3). Such processes at $I_0 \le I_c$ favor the relaxation of dot crystal defects in Si (vacancies and interstitial atoms), packing defects, shifts of dislocation lines, diminution of the cluster size in the near-contact Si area in solid phase. As is known, the effective thermal annealing of defects in chips is carried out at temperatures much below the melting point (T_m): for vacancies, $T = 0.2T_m$, for interstitial atoms, $0.05T_m$, for dislocations, $0.5T_m$ [8].

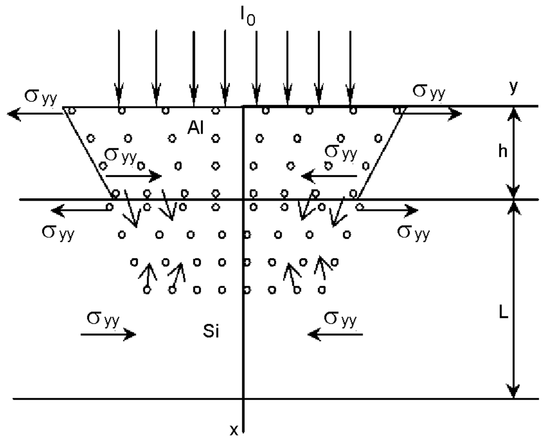

Fig. 3. Scheme of the crystal lattice strain in aluminum film and in the near-contact region of silicon in Al–Si contacts due to thermoelastic stresses σ_{yy} at the PLI of a metal-semiconductor contact at the intensity $I_0 < I_c$.

It is expedient to consider the quantitative assessments of thermoelastic stresses in Al–Si structures in the case when under local PLI, the stresses become developed at characteristic distances commensurable with the thickness of aluminum film and of the transition layer and are within the elasticity limits of the aluminum film. The maximum stress values at the MES interface in the absence of phase changes ($T < T_m$, I_0 ~

100 kW/cm^2) calculated using the procedure [8] amount $\sigma_{yy} = \sigma_{zz} = 6.7$–$8.1$ MPa and increase linearly with the irradiation intensity. The track of a neutral plane ($\sigma_{yy} = \sigma_{zz} = 0$) is located at a distance 35–40 μm from MES, and the signs σ_{yy}, σ_{zz} correspond to tensile stresses for Si at the MES interface and compressing ones at the non-working side of the structure. If there is no temperature gradient in the irradiated structure and the Poisson coefficients μ for separate layers are close together, it is possible to estimate radial σ_r and tangential σ_θ thermoelastic stresses at the Al–Si interface using the relations for two-layer structures [9]:

$$\begin{cases} \sigma_{hr} = \sigma_{h\theta} = -\dfrac{(\alpha_{T\mathrm{Al}} - \alpha_{T\mathrm{Si}})\Delta T}{(1-\mu)\left(\dfrac{1}{E_{\mathrm{Si}}L} + \dfrac{1}{E_{\mathrm{Al}}h}\right)}\left[\dfrac{1}{h} + \dfrac{(L+h)E_{\mathrm{Al}}x}{2(E_{\mathrm{Si}}J_{\mathrm{Si}} + E_{\mathrm{Al}}J_{\mathrm{Al}})}\right], \\ \sigma_{Lr} = \sigma_{L\theta} = \dfrac{(\alpha_{T\mathrm{Al}} - \alpha_{T\mathrm{Si}})\Delta T}{(1-\mu)\left(\dfrac{1}{E_{\mathrm{Si}}L} + \dfrac{1}{E_{\mathrm{Al}}h}\right)}\left[\dfrac{1}{L} + \dfrac{(L+h)E_{\mathrm{Si}}x}{2(E_{\mathrm{Si}}J_{\mathrm{Si}} + E_{\mathrm{Al}}J_{\mathrm{Al}})}\right]; \end{cases}, \tag{1}$$

where L and h are thickness of a silicon substrate and aluminum film, respectively; E_{Si} and E_{Al}, elastic moduli, J_{Si} and J_{Al}, inertia moments of sections of layers relative to the neutral line. Taking into account that $L \approx 300$ μm $>> h \approx 1$ μm, it is possible to take $E_{\mathrm{Si}} \sim E_{\mathrm{Al}}$, $E_{\mathrm{Si}}L >> E_{\mathrm{Al}}h$, J_{Si} and J_{Al} equal $J_{\mathrm{Si}} = hL^2/4$, $J_{\mathrm{Al}} = L^3/12$. Then the relations (1) become simpler:

$$\begin{cases} \sigma_{hr} = \sigma_{h\theta} = -\sigma_{0T}(1 + 6hx/L^2), \\ \sigma_{Lr} = \sigma_{L\theta} = \sigma_{0T}(h/L + 6hx/L^2), \\ \sigma_{0T} = (\alpha_{T\mathrm{Al}} - \alpha_{T\mathrm{Si}}\Delta T E_{\mathrm{Al}})/(1-\mu). \end{cases} \tag{2}$$

The estimated value of elastic stresses $\sigma_r = \sigma_\theta \approx 15.6$ MPa obtained for contact layer of silicon at a heating of structure on $\Delta T = 500°\mathrm{C}$ quite is according with a value $\sigma_{yy} = \sigma_{zz} = 8.1$ MPa, calculated on a procedure [8].

The experimental results and quantitative assessments of elastic stresses evidence the thermal mechanism of PLI effect at MES irradiation both from the metal side and through a silicon substrate. It is possible to explain some behavior features of defect systems under irradiation of an Al–Si structure through silicon, taking into account the dependence of radiation absorption coefficient in a semiconductor on its temperature. So, at $I_0 < I_c$, the $\lambda = 1.06$ μm radiation at the structure irradiation from the semiconductor side is absorbed mainly at the Al–Si interface. The I_0 increase up to $I_0 \approx I_c$ results in an increased temperature gradient at the interface and accelerated motion of the thermal front into the semiconductor. This promotes a fast heating of the semiconductor and increasing radiation absorption coefficient in the semiconductor. Thus, the back edge of radiation pulse does not achieve the Al–Si interface but is absorbed in the semiconductor bulk, and the structure is heated homogeneously. This process is similar to an usual thermal annealing. In this case, mechanical stresses at the Al–Si interface may arise only due to difference between the temperature expansion coefficients of materials, but the heating duration is already sufficient to provide the time for system relaxation, whereas at $I_0 < I_c$, mechanical stresses induced by the temperature gradient are increased due to difference in temperature coefficients of interacting materials. The further increase in I_0 results in that the energy becomes absorbed mainly in the subsurface layer of silicon and temperature gradients arising in the subsurface layer are so high that may cause a local or complete failure of the chip. The failure may have not only elastic but also fatigue [5] character. During the PLI experiments, the structures were observed to fail 2–3 s after the pulse action.

A similar effect at the specified intensity does not arise in the first SD group for two reasons: a) the energy absorbed in structure is different because of differences in reflection factors of aluminum ($R_{\mathrm{Al}} \approx 0.95$) and silicon ($R_{\mathrm{Si}} \approx 0.30$); b) a thin aluminum film of a thickness $h \approx 1$ μm on the surface of Si ($L \approx 300$ μm) becomes scaled or destroyed at considerable thermoelastic loads [4, 6]. Therefore, irradiation of an Al–Si structure at $I_0 < I_c$, corresponding to heating of aluminum contact and appearance of thermoelastic stresses at the Al–Si interface not exceeding the Al elasticity limit results in redistribution of the defect system in the very thin subsurface layer of silicon. Taking into account that thermal expansion coefficient of aluminum exceeds approximately 10 times that of silicon, the linear increase of the defect density at the edges of aluminum contact at an extension of the contact linear dimensions can be understandable. Using the concept of thermoelastic stresses [5, 8–10] at phase interfaces in the metal/semiconductor contacts, it is possible to explain abnormal diffusive profiles of aluminum in silicon [4–7].

When an aluminum-silicon structure is irradiated through a silicon substrate and the radiation is absorbed only at the interface, the stresses in silicon are developed similarly to the case of irradiation from the metal side but also here, those attain $\sigma_{yy} = \sigma_{zz} =$ 45–125 MPa at the same radiation intensity and, as is seen, may even exceed the highest permissible values for silicon, being $\sigma_{yy} \sim 100$ MPa [8]. The neutral surface track in this case is shifted towards the silicon free surface.

The temperature dependence of the radiation absorption coefficient in a semiconductor results in a qualitatively new stress distribution in a silicon plate. On the surface under irradiation, the compressive stresses up to about $\sigma_{yy} = \sigma_{zz} =$ 20–120 MPa are developed. The a neutral line track is about 5–10 μm from the silicon free surface.

It is possible to suppose that the thermoelastic stresses about 10–25 MPa at the metal/semiconductor interface will cause a rearrangement of structural-impurity defect systems in subsurface silicon layer and an activation of diffusion processes.

To conclude, the experimental results obtained confirm the model of the PLI thermal effect on MES with a Schottky barrier. The thermoelastic stresses arising in the Al–Si structures under the MES irradiation both from the side of metal plating and from that of the semiconductor may result in a redistribution of structural-impurity defects in the subsurface silicon layer in the absence of a melt at the Al–Si interface and in the chip failure. When applying the PLI of MES through the semiconductor substrate, it is necessary to take into account the possible dependence of the radiation absorption coefficient in a semiconductor from the material temperature at different wavelengths and mechanisms of the radiation interaction with the material. The thermoelastic interaction of layers in MES is confirmed by the dependence of a surface defect density and distance at which the defects are observed at the SD periphery on the radial size of contacts. The mechanically destroyed metal film at $I_0 > I_c$ may act as a getter of defects. The thermoelastic stresses in MES layers at PLI may activate the diffusion processes through the metal/semiconductor interface. The diffusivity values for interacting materials should differ in this case from the corresponding parameters for volume diffusion, as the specified process is carried out in a field of elastic forces at the interface.

As the metallographic examinations evidence, the laser-stimulated interaction in MES at the Al–Si interface makes it possible the formation of a nanosized structurized (perhaps porous) transition silicon layer due to relaxation of thermoelastic stresses in the subsurface silicon layer. It is to emphasize that all processes of the transition layer formation in this case also occur in the solid phase, as well as redistribution of structural defects at the periphery of the Schottky diodes. Of a specific interest are studies of electrophysical, optical, and luminescence characteristics of such a transition layer.

References

1. G.I.Vorobets, O.I.Vorobets, A.P.Fedorenko, A.G.Shkavro, *Functional Materials*, **10**, 468 (2003).
2. G.I.Vorobets, in: Frontiers Multifunctional Integrated Nanosystems, ed. by E.Buzaneva and P.Scharff, Kluwer Academic Publishers, Netherlands (2003), p.213.
3. G.I.Vorobets, M.M.Vorobets, T.A.Melnichenko, A.G.Shkavro, in: Physics and Technology of Thin Films, Proc. of IX Int. Conf., Misto NV, Ivano-Frankivsk (2003), v.1, p.191 [in Ukrainian].
4. V.I.Fistul, A.M.Pavlov, *Fiz. Tekhn. Poluprov.*, **17**, 854 (1983).
5. V.P.Veiko, Laser Treatment of Film Devices, Mashinostroenie, Leningrad (1986) [in Russian].
6. V.N.Abakumov, Zh.I.Alfyorov, Yu.V.Kovalchuk, E.L.Portnoy, *Fiz. Tekhn. Poluprov.*, **17**, 2224 (1983).
7. G.I.Vorobets, O.V.Nikulin, in: Physics and Application of Metal-Semiconductor Contact, Abstr. of All-Union Conf., Kiev Univ. Publ., Kiev (1987), p.50 [in Russian].
8. E.E.Kvasov, V.V.Makarov, *Fiz. Tekhn. Poluprov.*, **18**, 747 (1984).
9. V.S.Sergeev, O.A.Kuznetsov, N.P.Zakharov, V.A.Letyagin, Stresses and Strains in Microcircuit Elements, Radio i Svyaz, Moscow (1987) [in Russian].
10. B. Boly and D. Wainer, Theory of Thermoelastic Stresses, Mir, Moscow 1964 [in Russian].

Термопружні взаємодії в структурах Al–n–Si–Ni при імпульсному лазерному опроміненні

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Методами растрової електронної мікроскопії та оптичної металографії експериментально досліджено процеси формування та перерозподілу структурних дефектів у приконтактному шарі кремнію термічно невідпалених структур Al–n–Si внаслідок прояву термопружних напруг при імпульсному лазерному опроміненні. Виявлено формування структурованого перехідного шару на межі метал-напівпровідник при релаксації пружних напруг у металізації. Для пояснення особливостей поведінки систем дефектів на периметрі діодів Шотткі при опроміненні структур через кремнієве оптичне вікно запропоновано фізичну модель впливу лазерного проміння на контакт метал-напівпровідник, яка враховує температурну залежність коефіцієнта поглинання випромінювання у напівпровіднику.