Precision silicon doping with acceptors by temperature gradient zone melting

B M Seredin1, V V Kuznetsov, A A Lomov3, A N Zaichenko1 and S Yu Martyushov4

1Platov South-Russian State Polytechnic University, 132 Prosveshcheniya str., Novocherkassk 123456, Russia
2Saint Petersburg Electrotechnical University LETI, 5 Professora Popova str., Petersburg, 197376, Russia
3Valiev Institute of Physics and Technology of RAS Russia, 36/1 Nahimovskii prosp., Moscow 117282, Russia
4Technological Institute for Superhard and Novel Carbon Materials, 7A Centralnaya str., Troitsk 108840, Russia

Abstract. We present the results of optimization of the temperature gradient zone melting technique, also known as the thermomigration (ThM) technique, aimed on improvement of the quality of p-layers and formation of p-n junctions with sharper boundaries compared to those obtained by conventional thermal diffusion technique. In addition, ThM allows an expansion of the range of doping of silicon substrates with an acceptor impurity, usually limited by the solidus value. The ternary Al-Ga-Si and Al-Sn-Si melts were used as ligatures. The dependences of the migration rate of the liquid zones on temperature and composition for the Al-Ga and Al-Sn solvent metal are presented. The possibility of changing the acceptor concentration from $2\times10^{19}$ cm$^{-3}$ to $6\times10^{19}$ cm$^{-3}$ is shown. A threshold temperature of 1400 K was experimentally found for the ThM process with stable migration of triple liquid zones in a crystal. X-ray diffractional rocking curves and projection topography confirmed high structural quality of the Si(Al) p-layer with a thickness of 25 µm, obtained by ThM with stable moving liquid zones. The experimentally measured strain $\Delta d/d=2.3\times10^{-5}$ for the p-layer and the silicon substrate was used in the substitution model to estimate the Al concentration of $1\times10^{19}$ cm$^{-3}$. X-ray topographic images of the layers did not reveal both growth S-defects and misfit dislocations, confirming the high structural perfection of the layers and phase boundaries.

1. Introduction

Doping of Si and Al$_3$B$_4$ semiconductor wafers, provided by their local recrystallization due to the movement of the melt inside the wafer under the influence of the gradient of temperature (temperature gradient zone melting), is known as the thermomigration (ThM) technique. Current interest to the process of ThM increases both because of the fundamental nature of this phenomenon and due to the prospects of industrial application [1]. The ThM technique provides a possibility of formation of internal planar p-n junctions, as well as vertical channels of several tens of microns wide of arbitrary shape with sharp boundaries [2]. Such p-structures and adjacent p-n junctions can be applied in power electronics, photonics, biological sensors, micromechanical devices [3-5]. The formation of these structures by diffusion doping often does not satisfy the technical requirements and in some cases is
fundamentally impossible. Diffusion doping results in an extremely non-uniform distribution of impurities, and requires considerable time for the formation of layers and vertical channels, leading to blurring of their boundaries.

The ThM technique removes these problems. Another advantage of ThM technique is a possibility of predictable uniform doping of silicon with acceptor atoms with different concentrations. For example, the ternary Al-Ga-Si and Al-Sn-Si melts can be used as ligatures. The concentration of acceptors, aluminum or an aluminum based alloy used as a ligature, in recrystallized silicon is set by the solidus value in the Al-Ga-Si and Al-Sn-Si systems. To obtain the desired shape of the structure the stability of the liquid zone migration in the crystal must be ensured. However, the spontaneous emergence of local perturbations and their evolution at the crystal-melt interfaces leads to formation of growth defects in the crystal. In [6] the criteria were formulated for the dynamic stability of both the individual boundaries of crystallization and dissolution, and the interphase boundaries of growth and dissolution in the composition of the migrating liquid zone. The stability of the growth boundaries is significantly influenced by the zone migration rate, the magnitude of the temperature gradient, the uniformity of the thermal field along the sample surface, etc. [7]. The results of the X-ray double-crystal rocking curve analysis of structural perfection of 120 μm Si (Al) channels in a Si (111) matrix were presented for the first time in [8]. However, the majority of publications on the ThM technique deals with the possibility of various applications or with the theoretical analysis of the p-n junction arrays obtained using this technique [3, 4, 9-11].

This paper is devoted to a detailed study of the growth conditions of the ThM technique with the goals of extending the range of doping of silicon substrates with an acceptor impurity based on Al, Ga and their alloys with Sn, and determination of the structural perfection of the formed layers.

2. Experiment

For fabrication of a planar p–n junction by ThM technique we used two n-type Si(P)(111) single-crystal wafers (ρ = 10 Ω-cm, 40-100 mm diameter and 500 μm thickness), later called substrate and source wafers. The solvent was prepared of aluminum of A999 grade as the zone-forming material on the growth surface of the sample. The flat liquid zones were formed by capillary drawing of the melt [7] into the gap between the source and the substrate wafers. Before the process the wafers passed the standard mechanical and chemical treatment. Capillary gap thickness was set in the range from 2 to 50 μm using three bumps on the periphery of the source wafer. Before the process the wafers passed the standard mechanical and chemical treatment. Capillary gap thickness was set in the range from 2 to 50 μm using three bumps on the periphery of the source wafer. The local liquid zones were formed by forced wetting of the Si substrate with Al-Ga and Al-Sn solvent in a temperature range of 1100–1150 K. The solvent composition varied with the x_{Al} interval equal to 0.1 at. ratio. The subsequent process of ThM of the liquid zone through the silicon wafers was carried out in a vacuum unit in the field of temperature gradient from 20 to 100 K/cm. The temperature of the ThM process was varied from 950 to 1550 K. The zone migration rate was measured indirectly using the metallographic analysis of the transverse thin sections of recrystallized layers by the growth bands created by thermal pulses at given time intervals [2].

The dopant concentration in the ThM recrystallized layers was determined using CV profilometry on a Wafer Profiler CVP-21 doping profile measurement machine (WEP, Germany) [12].

The structural characterization of the silicon layers and channels recrystallized during the ThM process was carried out using the X-ray diffraction topography and double-crystal rocking curves techniques. The dislocation-free substrates were selected for these studies. A ~50 μm thick ThM Si(Al) layer under temperature gradient about 90 K/cm was fabricated with a tungsten heater located on the back side of the source wafer. After the process the outside part of the source wafer was removed by milling and chemical etching so that both Si(Al) film and pure Si substrate were revealed. As a result of the processing, a wedge with an inclination of ϕ=1 deg to the (111) crystal planes of the substrate was formed on the sample surface. Such a structure allows study of the structure of the ThM Si (Al) layer without the influence of artifacts introduced during sample preparation. The X-ray projection topograms were obtained by the Lang method using an XRT100 CCM setup (Rigaku Co.) with a rotating silver anode (0.056nm). To make a topogram an X-ray beam was directed to the back
surface of the sample. The parameter of shooting was \( \mu t = 0.36 \), where \( \mu \) is the linear coefficient of photoelectric absorption (8 cm\(^{-1}\)) and \( t \) is the sample thickness. The experiments on X-ray rocking curves with parallel \((n,-n)\) setting were carried out on a TRS-1 diffractometer (SCB Shubnikov IKAN, USSR). A flat perfect Si(111) single crystal was used as a crystal monochromator. The rocking curves of the (333) Bragg reflection (CuK\(\alpha\) radiation) from the investigated samples were measured by \( \Delta \theta = 9 - 9\theta_B \) (\( \theta_B \) – Bragg angle) sample crystal rotation with a step of 0.5 arc s.

3. Results and discussion

3.1. The migration speed of the liquid zone

Figure 1 shows the experimentally obtained temperature dependences of the migration rate \( \nu \) of liquid zones for the Si-Al-Ga and Si-Al-Sn systems.

![Graphs showing migration rate vs temperature for Si-Al-Ga and Si-Al-Sn systems](a) and (b)

Figure 1. Migration rate \( \nu = \nu(T, x) \) of liquid zones with solvent metal Al\(-\)Ga\(_{x-1}\) (a) and Al\(-\)Sn\(_{x-1}\) (b) when changing the composition in \( x_{Al} \) from 1 to 0 with a step \( \Delta x_{Al} = 0.1 \) and \( n = 1 - 11 \), respectively (n is the number of the curve in figure).

The authors of [2] show that for binary systems the migration rate of the liquid zones follows the equation:

\[
\nu = \nu_0 \exp\left(-\frac{\Delta H}{RT}\right)
\]

where \( \nu_0 \) is a constant; \( \Delta H \) is the activation energy of the ThM process. The obtained results show that the ThM rate for the Si-Al-Ga and Si-Al-Sn systems follows the equation (1). With changing the composition of the solvent from \( x_{Al} = 1 \) to \( x_{Al} = 0 \) the activation energy for Si-Al-Ga increases from 180 to 460 kJ/mol, while for Si-Al-Sn it decreases to 80 kJ/mol (see figure 1).

The obtained results show that the minimal (threshold) temperature for the ThM process \( T_{th}(x_{Al}) \) significantly exceeds the temperature of formation of the liquid zone. An increase of contents of the third component, Ga or Sn, in the zone results in an increase of the \( T_{th} \) from 1213 K to 1373 K and to 1323 K, respectively. The dependences of the ThM rate of the composition of the melt Si-Al-Ga and Si-Al-Sn are presented on figure 2.
Figure 2. Dependence of the ThM rate on the composition of the solvent zone for $T_1=1223(1)$; $T_2=1273(2)$; $T_3=1323(3)$; $T_4=1373(4)$; $T_5=1448(5)$; $T_6=1473(6)$; $T_7=1493(7)$ (K). The solid curves are Si-Al-Ga; dotted - Si-Al-Sn.

Figure 3. Density $N_{br}$ of local discontinuities of the flat zone as a function of temperature (capillary with a thickness of $l = 50 \mu m$) and the solvent Al$_x$-Ga$_{1-x}$ zones. $x = 1(1); x = 0.8(2); x = 0.5(3); x = 0.2(4)$ and $x = 0$ (5).

Their behavior is described by the equation for binary systems [2]:

$$\nu = \frac{D^I G^I dC_2^I}{C_2^I - C_1^I} dT,$$

where $D^I$ is the coefficient of interdiffusion of the components in the melt, and $G^I$ is the temperature gradient in the melt. Adding gallium to the liquid zone changes all factors in the presented expression, with the highest influence on the values $C_2^I - C_1^I$ and $dC_2^I/dT$. For example, for the Si-Al-Ga system at temperatures below 1473 K an increase of Ga concentration in the zone leads to a decrease in the rate $\nu$ due to a decrease in the solubility of Si in the melt. At temperatures above 1473 K, a multiplier becomes dominant in accordance to the phase diagram, and the zones with high Ga content migrate faster. Thus, the most influential factor on the rate of ThM (Figure 2) is the ratio of the concentration gradients of the liquid phase at the selected temperature, determined by the slope of the liquidus dependence.

The stability of ThM, estimated from the density of local discontinuities of the flat layer of the liquid phase $N_{br}$ (Figure 3), was experimentally investigated in the entire range of compositions of the liquid zones. An increase of the temperature reduces the number of gaps in the flat zone and, thereby, improves the quality of the recrystallized layers. The zones enriched with gallium require higher temperatures to ensure the structural perfection of the formed layers.

3.2. C-V profilometry

Figure 4 shows the dependence of the concentration of an electrically active impurity (acceptor) in the ThM p-type Si (111) (Al$_x$-Ga$_{1-x}$) layers on the solvent composition $x_{Al}$ at the temperatures of 1373 and 1448 K. At the applied temperatures an increase in the contents of Ga in the solvent leads to an increase of the concentration of acceptors. The concentration $C_a$ shows a quasi-logarithmic nature and can be precisely tuned in the range from $2 \times 10^{19}$ cm$^{-3}$ to $6 \times 10^{19}$ cm$^{-3}$. 
3.3. X-rays diffraction study

All samples were treated with selective acid etching to find the relation between the structural defects of the formed ThM layers, the defects of the original silicon wafer, and the conditions of the ThM process. The etching results show that dislocations are the standard kind of structural defects in the recrystallized layers. No dependence of the dislocation density on the composition of the liquid zone was found. For the X-ray diffraction experiments, the dislocation-free wafers were selected.

Figure 5 shows the image of a part of the 0-4 4 reflection projection topogram from a standard Si wafer doped by Al under a temperature gradient. The right part (S) of the image shows the initial wafer 300 µm thick, not influenced by the doping agent, with only few small residual defects from surface treatment visible. The central part (F) refers to the initial substrate with a 25 µm layer of Si source wafer, which underwent the Al doping. In the center of this part an agglomerate of larger defects can be seen. They may be associated with the local breaks in the Si (Al) layer during its growth or may be caused by the subsequent preparation of the sample for research. Still we can conclude that the sample shows good crystal quality. The left part (H) is an area with Si(Al) layer above the previous Si layers and the number of defects is significantly higher.

Figure 5. Part of the projection Lang topogram of Al ThM-doped Si(111) n-type wafer under a temperature 1450 K for 10 min.

Figure 6. DCD rocking curves from the original Si(111) part (S) and from the ThM Si(Al)/Si(111) structure (F).

These observations were supported by the X-ray double-crystal diffraction (DCD) rocking curves. An example of DCD curves from Si substrate part (S) and Si(Al) layer on the substrate (F) are shown in figure 6. The DCD curve from the substrate part (S) demonstrates full width half maximum (FWHM) equal to 3.3 arc s. This proves high perfection of the original silicon wafer and an absence of noticeable number of dislocations (the theoretical FWHM value for an ideal crystal is 2.63 arc s [13]). The curve (F) from the Si(Al)/Si(111) structure shows two narrow (4 arc s) peaks: from the Si(Al) layer at ∆θ=-5 arc s, and from the substrate (S) at ∆θ=0. The increase of the widths of the peaks compared to the width of the peak for the original substrate is a result of sample deformation due to the variation of the lattice constant in the Si(Al) layer. The difference of the measured angular widths of the peaks gives the value of lattice variation ∆d/d=2.3×10⁻⁵ in the first approximation. This value...
allows estimation of the Al concentration in the film of $\sim 1 \times 10^{19} \text{cm}^{-3}$, using the substitutional model [14], which does not contradict the data of the CV profilometry. The geometrical features of the sample did not allow to perform the complete diffraction analysis and to resolve the actual lattice parameter. Additional studies of the aluminum content in the Si (Al) layer by the SIMS method were performed and the concentration value of $0.95 \times 10^{19} \text{cm}^{-3}$ was obtained [15], in a good agreement with the X-ray analysis data.

4. Conclusion
The thermomigration (ThM) processes in Si (111) n-type layers were studied, the concentration and temperature dependences of the liquid zones migration rate (Si-Al-Ga) were obtained. The dependences of the zone migration rate on the temperature of the ThM process can be described by exponential functions. With changing the solvent composition from $x_{\text{Al}} = 1$ to $x_{\text{Al}} = 0$ the activation energy of ThM increases from 180 to 460 kJ/mol for the Si-Al-Ga composition, but for Si-Al-Sn composition it decreases to 80 kJ/mol. The migration rate of the Al-Ga zone in silicon with increasing gallium content at temperatures below 1473 K decreases, while at higher temperatures it increases. The threshold temperature for the start of a stable ThM process in Si with an increase in the concentration of Ga in the temperature range from 1213 to 1373 K monotonously increases. An increase in the concentration of gallium in the melt leads to an increase of the concentration of an electrically active impurity in silicon.

The methods of double-crystal X-ray diffractometry and X-ray topography were used to study the structure of aluminum ThM-doped Si (Al) layers and Si (111) substrates. It is shown that the structural perfection of the ThM layers is significantly influenced by the dislocation density in the initial substrate wafer. The magnitude of the deformation in the Si (Al) layer and the Al concentration in the substitution model are, respectively, $\Delta d/d = 2.3 \times 10^{-5}$ and $1 \times 10^{19} \text{cm}^{-3}$.

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