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Thermodiffusion Applications in MEMS, NEMS and Solar Cell Fabrication by Thermal Metal Doping of Semiconductors

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Abstract: In this paper recent advances pertinent to the applications of thermodiffusion or thermomigration in the fabrication of micro and nano metal-doped semiconductor-based patterns and devices are reviewed and discussed. In thermomigration, a spot, line, or layer of a p-type dopant, such as aluminum, which is deposited on a semiconductor surface, penetrates into the semiconductor body due to the presence of a temperature gradient applied across the wafer body. The trails of p-doped regions within an n-type semiconductor, in the form of columns or walls, may be used for several applications, such as the isolation of a part of a semiconductor device, the formation of conductive channels within a silicon block, the fabrication of three-dimensional arrays for biological applications, manufacturing of solar cells, manipulation of material properties, and so on.

Keywords: Thermomigration, Thermodiffusion, Soret effect, Semiconductor devices, Micro-electro-mechanical systems (MEMS), Nano-electro-mechanical systems (NEMS), Solar cells, P-n junctions, Three-dimensional arrays, Opto-electronic sensors

1 Introduction

Thermodiffusion or the Soret effect is the process of mass diffusion driven by a temperature gradient across a gas, liquid or solid mixture. It may be present in the form of pure diffusion in various mixtures from hydrocarbons to molten metals and salts [Eslamian, Sabzi, & Saghir (2010); Huang, Chakraborty, Lundstrom, Holmden, Glessner, Kieffer & Lesher, (2011)] or combined with convective flows [Podolny,

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Nepomnyashchy & Oron (2010); Yan, Jules, & Saghir, (2007); Jaber, Khawaja & Saghir (2006)]. In semiconductor and metal mixtures and crystal growth literature it is often referred to as thermomigration or sometimes thermotransport [Van Vaerenbergh, Garandet, Praizey, & Legros (1998); Eslamian & Saghir (2010)]. Due to the increasing application of thermodiffusion in the fabrication of semiconductor micro-electromechanical systems (MEMS), nano-electromechanical systems (NEMS) and micro and nano thin films and features, the present paper reviews the recent advances and patents that employ thermodiffusion to fabricate the aforementioned devices. A recent review of experimental methods and results in thermodiffusion has been performed by Srinivasan and Saghir (2011). Also due to the fundamental complexity associated with thermodiffusion experiments on the ground and in the presence of gravity, many thermodiffusion experiments have been performed onboard the International Space Station and during other space missions, e.g. [Shevtsova (2010); Van Vaerenbergh, Garandet, Praizey, & Legros (1998)].

Thermomigration is a physical phenomenon that is present in a process called temperature gradient zone melting (TGZM) that was initially introduced as a crystal growth method by Pfann (1969). TGZM has been used to grow semiconductors such as GaP and ZnTe (Oda 2007), however, it is more considered as a route for modifying and doping semiconductors in several MEMS applications.

Figure 1 schematically depicts the TGZM process. First a layer, spot, or any desired pattern of a dopant metal such as aluminum is formed on the bottom surface of a thin silicon wafer. Then the top surface of the wafer is heated, for instance, using heat radiation from the top; simultaneously heat is removed from the bottom surface in order to help a temperature gradient to be established across the silicon wafer. The most common combination of semiconductor and metal is the silicon-aluminum system. The melting point of aluminum is 660 ˚C, whereas that of silicon is 1414 ˚C with a eutectic temperature of 577 ˚C (Murray and McAlister 1984). The film temperature should be high enough ($\sim$1000 ˚C) to produce a moving aluminum-silicon molten zone on the cold surface. Once aluminum is melted, it dissolves some silicon forming a molten aluminum-silicon zone on the cold surface. Owing to a global temperature gradient across the silicon wafer ($\sim$10 ˚C), a local temperature difference (0.1 ˚C) is established across the molten zone (1 μm). Silicon atoms dissolved in aluminum move downward towards the lower end of the melting zone, which is in contact with the solid phase. At this interface, a dilute mixture of aluminum in silicon crystallizes and precipitates leaving a solid aluminum-doped silicon layer behind while the melting zone continues to migrate upward. Therefore, molten aluminum works as a silicon carrier in this process, as in the solid phase, it is only slightly soluble in silicon, and therefore the formed solid phase in the rear of the melting zone contains a slight amount of aluminum that is enough to make a p-doped zone and a p-n junction within the n-silicon wafer. The rest of this paper is devoted to description and discussion of several applications of thermodiffusion in the design and fabrication of semiconductor related devices. This includes p-n junction isolation, fabrication of conductive passages, the formation of channels and trenches, fabrication of three-dimensional arrays, preparation of solar cells and material property manipulation in micro and nano electromechanical devices. Theory of thermodiffusion in molten semiconductors and metals may be found in [Eslamian, Sabzi, & Saghir (2010); Eslamian & Saghir (2010)]. Here, recent advances and patents pertinent to each application are reviewed from a materials fabrication point of view. A good review on the use of thermodiffusion in several MEMS devices is also provided by Buchin and Denisenko (2006). Figure 2 summarizes various areas of research in thermodiffusion. It also shows some of the thermodiffusion applications in metal-semiconductor mixtures that are considered in this paper.

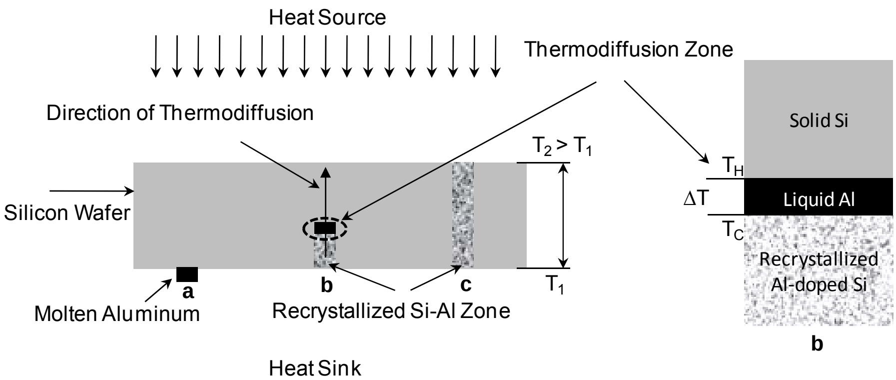


Figure 1: (a) Schematic illustration of thermodiffusion in Temperature Gradient Zone Melting (TGZM) method. Beginning of the process wherein an aluminum layer is melted due to the surface temperature of the cold surface T_C (a); the molten aluminum dissolves silicon and migrates towards the hot surface T_H, leaving behind a recrystallized column (b); an aluminum-doped silicon column is formed extending from the cold side to the hot side of the silicon wafer (c); on the right side the magnified thermodiffusion zone (b) is shown.

2 P-N Junction Isolation

P-n junctions are made in semiconductors to increase the breakdown voltage and reduce the leakage current in high power devices. It may be also interpreted as

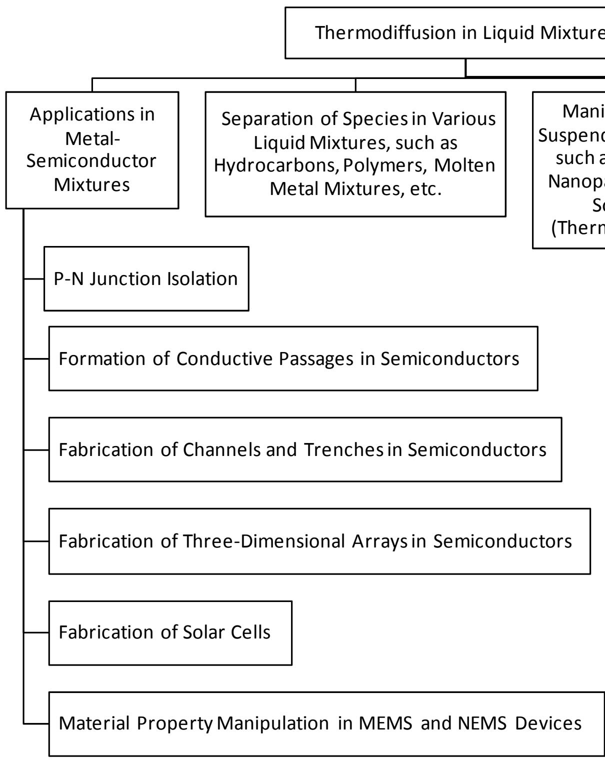
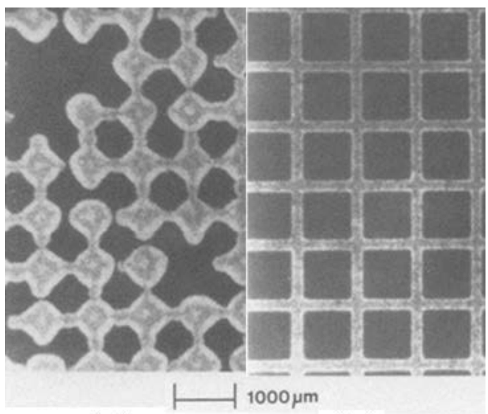


Figure 2: Various areas of research in thermodiffusion. Some of the thermodiffusion applications in metal-semiconductor mixtures are shown also.

a method to isolate electronic components in an integrated circuit or a MEMS device by surrounding the components using p-n junctions. Several isolation methods have been proposed; local isolation may be achieved through the local oxidation of silicon on a semiconductor substrate and forming an isolation region on a wafer [Kim and Pan (1992)]. When isolating of the entire thickness of a wafer from top to the bottom is concerned, molecular diffusion of a dopant in the semiconductor body at a high uniform temperature is the conventional method employed to accomplish the p-n junction isolation. Alternatively, thermomigration has been suggested for the formation of p-n junctions in the entire body of a silicon surface [Buchin and Denisenko (2006)]. It is a rapid and low thermal budget process. In fact the fabrication of p-n junctions in semiconductor bodies is one of the earliest applications of thermomigration in semiconductor devices [Cline and Anthony (1976a), (1977)]. The method is flexible also in that various kinds of p-n junctions may be formed. For instance, Anthony and Cline (1976b) patented a process for multiple p-n junction formation with an alloy droplet. In this process, a droplet containing two or more doping elements with a different ratio of diffusivity is thermomigrated through a body of semiconductor material, leaving behind a recrystallized region containing at least two dopant materials. The slower diffusing dopant species is largely left behind in the region to form a region of conductivity type determined by the slower diffusing species while the faster diffusing species will diffuse outward and form an annulus around the recrystallized region of a conductivity type determined by the faster diffusing species. The original semiconductor material of the body will form a third conductivity type region. With three dopants of different diffusivity in the alloy droplet, it is possible to produce four regions of different type conductivity (including the original body of semiconductor material) with a single droplet thermomigration. For details of this process please see the patent by [Anthony and Cline (1976b)].



(a) (b)

Figure 3: Effect of the ambient gas on the quality of the thermomigrated regions at the exit side of the substrate. (a) Process at the presence of air, where discontinuity and smearing is visible; (b) process at the presence of 1% O_2in argon, where continuous and perpendicular grid lines are formed [Lischner, Basseches, D'Altroy (1985)].

Since the introduction of the thermomigration method for the formation of p-n junctions, various workers have studied the characteristics of the doped areas. Lischner, Basseches, D'Altroy (1985) used thermomigration to form a 40 mm thyristor with isolation square-shape grids. They studied the motion of the molten zone, breakup and smearing of the molten zone, etc. Their experiments show a significant effect of the gas ambient on the precise control of the straight motion of the melt with no smearing of the pattern at the exit surface of the wafer. When the process is performed in a 1% O_2 in argon instead of air atmosphere, a nice grid of isolating regions is formed with minimum distortion and smearing (see Figure 3).

Nagel, Kuhlmann, Sittig (1996) attempted to reduce the processing time and thermal budget used in a Rapid Thermal Process (RTP) reactor. The application of a temperature gradient and the thermomigration process in their work is not explicitly mentioned, but it is implied that in their method use is made of the thermodiffusion phenomenon to speed up the diffusion process. They produced p-n junctions using aluminum-doped silicon wafers with blocking capabilities beyond 2.5 kV. Dilhac, Morillon, Ganibal & Anceau (2001) used the RTP apparatus combined with thermomigration process and studied the process control and the end-point detection of the isolation junctions during thermomigration of aluminum in silicon. They optically detected the emergence of the molten zone from the end of a rotating silicon wafer, using laser light reflectometry. Laser aims at a spot on the wafer surface; due to a difference between the optical properties of the silicon surface and those of the emerged aluminum-silicon lines, a change in the intensity of the reflected laser light is considered as the end of the thermomigration process.

Chung and Allen (2006) studied electrical isolation of bulk-micromachined single crystal silicon (SCS) MEMS devices using through-wafer n-p-n junction isolation via thermomigration. The n-p-n regions electrically isolate various regions of the SCS from one another by acting as series connected back-biased diodes. In their work, an electrostatic actuator with thickness of 300 μm was fabricated from a single silicon wafer with a breakdown voltage of single thermomigrated n-p-n junction of 189 V with a leakage current less than 70 nA. For multiple junctions in series, overall breakdown voltages were greater than 1500 V. Figure 4 shows the current-voltage behavior of 12 n-p-n junctions in series.

To further demonstrate the capability of the thermomigration process, Chung and Allen (2006) fabricated an actuator from a single silicon wafer. A scanning electron micrograph (SEM) of the front of the device is shown in Figure 5. The actuator is a rotary device that is divided electrically into inner and outer portions by thermomigrated aluminum. Three of the four beams have two thermomigrated areas each. The actuator is contacted on a probe station with a tungsten probe contacting the stator and another probe contacting the rotor. The probes are driven by a high-voltage amplifier. The amplifier is driven by a function generator with a sinusoidal signal output. An oscilloscope is connected in parallel to the probes to monitor the voltage across the device. At the voltage just below the break down, the actuator displacement was measured optically to be approximately 15 μm at a radius of 1.5 mm.

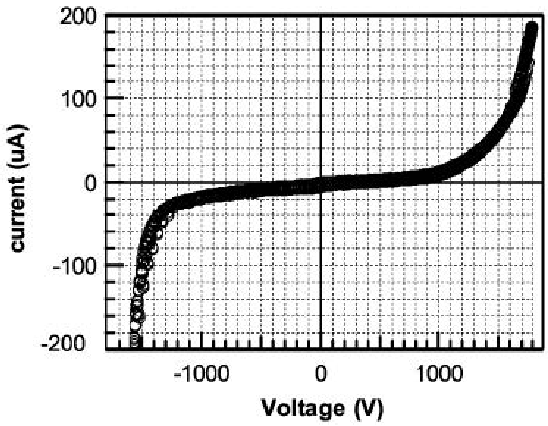


Figure 4: Current-voltage curve for 12 n-p-n junctions in series. The breakdown voltage is about 1500 V with a leakage current of less than 10 μA for voltages less than the breakdown voltage [Chung and Allen (2006)].

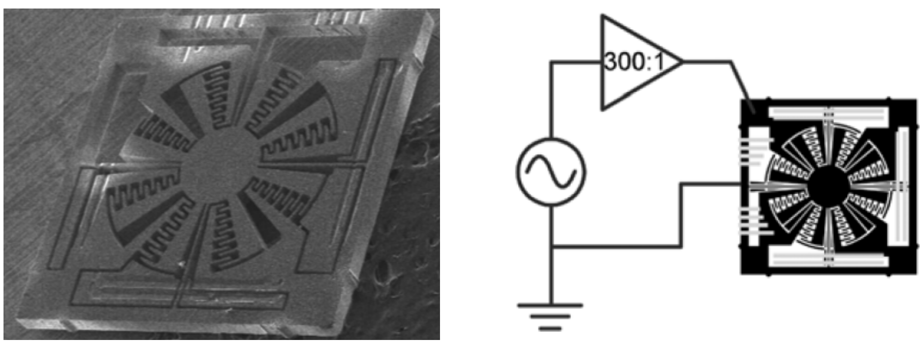


Figure 5: (a) SEM of a rotary actuator made by thermomigration. The overall chip dimensions are 4.5 mm $\times$ 4.5 mm $\times$ 0.2 mm. The beams measure 30 μm $\times$ 1.5 mm $\times$ 200 μm. (b) Electrical model for the actuator. The actuator is divided electrically into an inner (rotor) and outer (stator) portion. The stator is driven by a sinusoidal signal that is amplified 300:1 [Chung and Allen (2006)].

Allen and Chung (2006) patented the above-mentioned fabrication method of a micromachined device having electrically isolated components. The summary of this patent is as follows: a movable component is formed within a substrate via a suitable micromachining technique. Further, thermomigration technique is utilized to change the electrical properties of the substrate in a region separating the movable component from other portions of the substrate. The electrical properties of this region are changed such that the region electrically insulates the movable component from the other portions of the substrate. Thermomigration is used to dope regions of a semiconductor, thereby changing the electrical properties of the doped regions. To do so, a p-dopant is deposited on the surface of an n-doped silicon layer. Thermomigration of the aluminum through the silicon layer forms a p-type region in the layer. This p-type region may be used as a conductor between the substrate and a device formed on the surface of the layer. However, conductive regions formed via thermomigration techniques typically exhibit relatively high capacitance when current is passed through the conductive regions. This high capacitance reduces the speed at which signals can be communicated through the conductive regions. Since thermomigration enables a relatively thick layer to be quickly and efficiently doped through the entire thickness of the layer, it provides a practical and efficient methodology for junction isolation within most MEMS devices, particularly those with movable components that should be electrically isolated. Furthermore, since the movable components of most MEMS devices move at slow speeds relative to commonly used electrical signal frequencies, the capacitance issue is not a significant limiting factor in the present application.

In the preferred embodiment, an n-type semiconductor substrate, such as a single crystal silicon (SCS) substrate, at least approximately 25–50 microns suitable for many applications (e.g., the fabrication of high sensitivity, low noise MEMS gyroscopes and accelerometers) is used. A dopant is formed on the substrate via any suitable micromachining process (e.g., electron beam deposition). After the formation of the dopant, it is thermomigrated through the substrate. In this regard, the bottom surface of the substrate is heated to create a thermal gradient through the substrate. After thermomigration of the dopant, at least one movable component is formed in the substrate through any suitable micromachining technique. The movable component should be formed in one side of the thermomigrated junction so that it is electrically isolated from the other side of the junction. For example, in the embodiment shown by Figure 6, a spring, a rotor, and a stator are etched into the left of the junction. The spring and rotor are movable with respect to stator. As a result of the foregoing methodology, the right side of the junction provides mechanical support for each of the components on the left side but is electrically isolated from each of them. Such electrical isolation is achieved without compromising the mechanical integrity of the substrate. A gap exists between the rotor and stator, and the stator is electrically isolated from the spring and the rotor. As a result, any voltage difference applied across rotor and stator should not be shorted out by the right region depending on the material of the rotor and stator, the size of the gap between rotor and stator, and the amount of voltage difference applied to the rotor and stator. Such a voltage difference, therefore, may cause the rotor to move with respect to the stator.

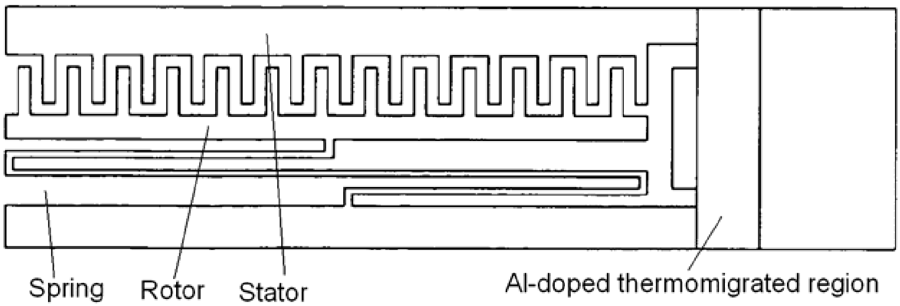


Figure 6: Isolating the left-side components (spring, rotor and stator) from the right-side region of the semiconductor body using an n-p-n junction formed by thermomigration [Allen and Chung (2006)].

3 Formation of Conductive Passages in Semiconductors

The formation of conductive channels that provide electrical connection between two components is another practical application of thermomigration in semiconductor devices. Here only recent work is reviewed among many others.

In a patent by Kriegel, Kudella & Arnold (2001), a procedure is proposed to form conductive channels to connect two surfaces through forming a thermomigrated column in the body of a semiconductor wafer, which may be used as an optoelectronic sensor. The section of such sensor component is shown in Figure 7. It is a semiconductor component consisting of silicon and has a wide n-conducting layer ($\sim$300 μm). On the front surface, a thin p-conducting layer ($\sim$ 0.55 μm) extends. Between the two semi-conducting layers, a depletion region forms that is used to produce electron-hole pairs. The front side is coated with an anti-reflection layer and is structured through insulating layers, such as silicon dioxide. Electro-magnetic radiation encountering the outer surface area goes through the p-conducting layer into the depletion region where it is largely absorbed forming electron-hole pairs. The depletion region divides these carrier pairs; electrons flow to the n-side, holes flow to the p-side. To measure this photo-flow, which is a measure for the radiation efficiency, the main body must be integrated into a suitable electric switch. To do so, on its rear-side outer surface structured through insulating layers, there are electrodes with flat contact points. The rear-side outer surface is formed from an outer surface of the n-conducting layer itself.

To position the connection electrode of the p-conducting layer also on the rear-side outer surface of the main body, a cylindrical semi-conducting channel of the p-type extends from the p-conducting layer to the rear-side outer surface. The p-conducting channel is produced by means of thermomigration. The rear-side end of this junction is surrounded by an additional p-conducting area to facilitate a faultless contacting of the p-conducting layer via the cylindrical area and the electrode. Since the electrodes of the n-conducting layer and the p-conducting layer are lying next to one another on the rear-side outer surface, the main body can be easily connected to a circuit board and integrated into an electric switch.

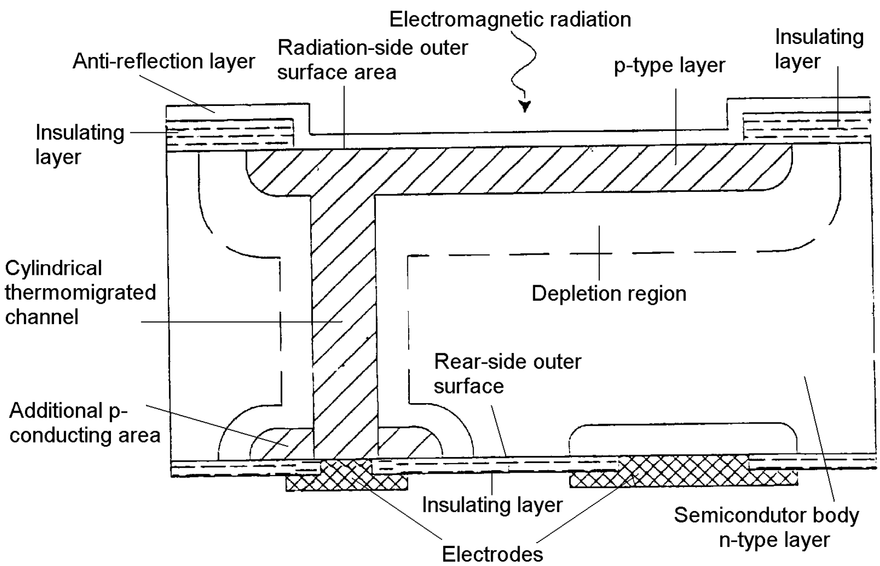


Figure 7: An opto-electronic sensor made out of a semiconductor body incorporating a conduction channel made by thermomigration [Kriegel, Kudella & Arnold (2001)].

Zelsacher (2003) patented a process for fabricating three-dimensional circuits with electrically connected semiconductor chips. In this invention, semiconductor chips are stacked one above the other and are connected through conductive channels between mutually opposite surfaces of the chips by thermomigrating a conductive material.

Figure 8a displays a plan view of an n-doped silicon chip having a surface to which aluminum has been applied and patterned. This patterning process is followed by an RTP process, where a temperature gradient is produced in the silicon chip. Deposited aluminum then propagates along the temperature gradient into the depth of the silicon chip and thus forms pillar-type p-conducting channels of interconnects. According to the process, aluminum is patterned such that this p-conducting region surrounds an n-conducting region forming a pillar-type n-conducting channel, which is led between the two surfaces of a silicon chip, where the n-conducting region is electrically insulated from other zones of the chip by the p-conducting region.

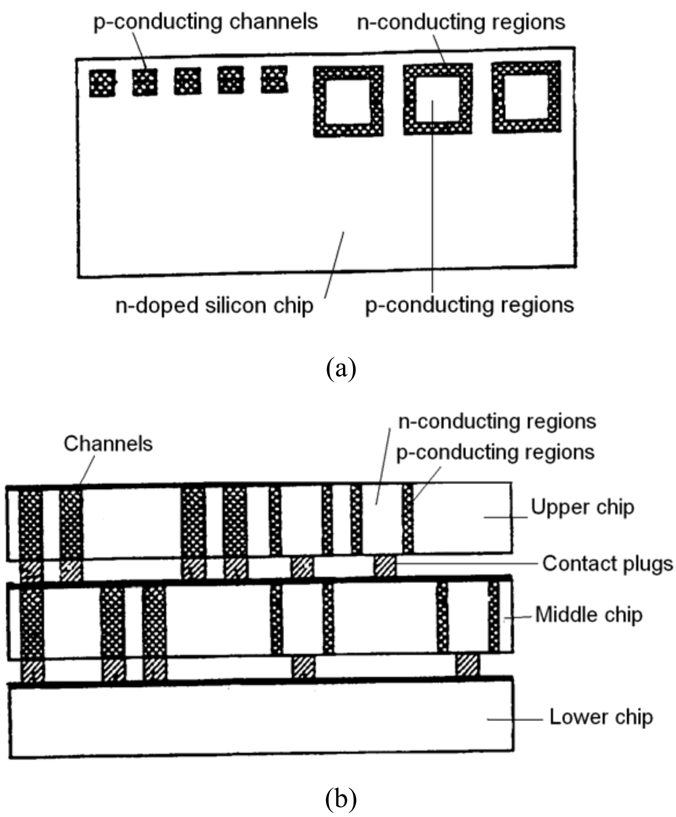


Figure 8: (a) Formation of three-dimensional conducting channels in a semiconductor, (b) connecting three chips using thermomigrated contact plugs [Zelsacher (2003)].

In the exemplary embodiment shown in Figure 8b, three semiconductor chips used in computers are shown, named as lower, middle and upper chips. The middle chip on its top side has contact plugs with pattern that correspond to the pattern of the channels and conductive regions on the rear side of the upper chip. In a similar manner, on the active top side of the lower chip, such contact plugs are provided for electrically connecting the rear side of the middle chip. To produce those interconnects through semiconductor chips in a three-dimensional circuit arrangement thermomigration was proposed.

4 Fabrication of Channels and Trenches in Semiconductors

The development of high aspect ratio micromachining processes provides opportunities for the extension of three dimensional technologies that may be used for the integration of passive and active electronic devices and sensors. Among several existing methods, deep reactive ion etching (DRIE) with halide containing gases, and etching in alkali solutions are currently the two dominating silicon anisotropic etching techniques. However due to the cost and several other restrictions of these methods, thermomigration based processes for the formations of trenches is also considered as an alternative [Gautier, Ventura, Jérisian, Kouassi, Leborgne, Morillon & Roy (2006)].

Fabrication of through channels in semiconductors using the thermomigration method has basically two main steps: first to form a p-doped region within an n-type semiconductor with any desired shape, and then to use an etchant so as to remove the formed region without affecting the main body of the semiconductor. Buchin, Denisenko & Rudakov (2002) and Buchin, Denisenko, and Simakin (2004) introduced this application and formed through channels by post-processing of the doped regions via etching. In one case [Buchin, Denisenko & Rudakov (2002)], the initial wafer with electron-beam deposited, 3-mm-thick $60 \times 40\ \mu$m rectangular aluminum spots, was heated from rear side up to a temperature of 1100 ˚C. The temperature of the front side, on which the melted zone entered the substrate, was 8-10 ˚C lower due to conduction heat transfer with the water-cooled copper holder. The thermal migration time was about 25 min and the process termination was detected using a pyrometer. Selective ionic etching was performed in a vertical Teflon electrochemical cell to clear the channels with an etching rate of 5 μm/min. In a second example [Buchin, Denisenko, and Simakin (2004)], silicon wafers with a thickness of 460 mm were used and 2 to 5 mm thick aluminum pads of various shapes were formed on the substrate. Infra Red (IR) heating source was used to perform the thermomigration. Selective chemical etching was employed to remove the p-doped region. It was observed that channels possess an inhomogeneous structure with two distinct shells with different physicochemical properties at the periphery of each channel. These shells may significantly influence the characteristics of p-n junctions in the channels.

Gautier, Ventura, Jérisian, Kouassi, Leborgne, Morillon & Roy (2006) used double-side polished 6 inch float zone phosphorous-doped wafers with a high resistivity, a (100) crystalline orientation, and a thickness of 240μm. An aluminum grid was patterned on one side of the sample with two metal stripes of 50μm wide and spaced with 100μm. The thermomigrated samples were etched electrochemically where process parameters were varying so as to obtain optimum conditions. The maximum etch velocity was 22μm/min for a maximum available current of 20 A. It was concluded that the method is competitive with deep reactive ion etching (DRIE). Figure 9 shows symmetrical trenches or porous regions on both sides of the wafer, where the polarity was inverted during the anodization process.

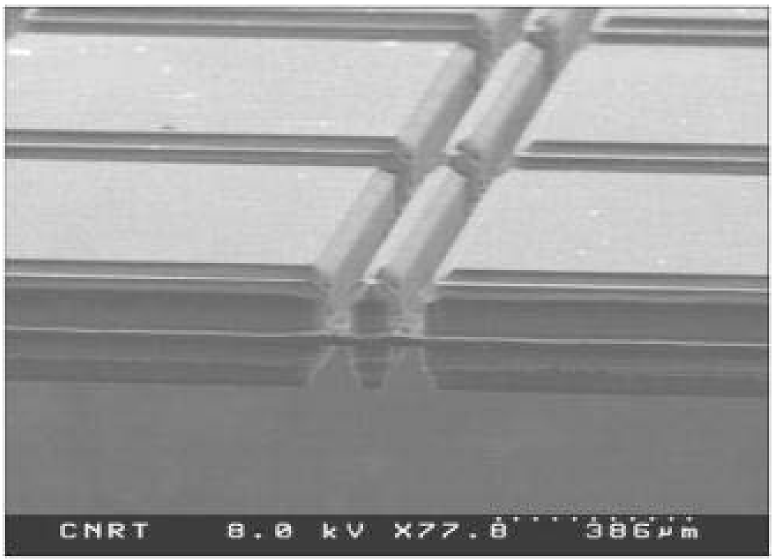


Figure 9: SEM image of trenches produced by thermomigration on both sides of a wafer. Current density used was 29mA/cm^2 applied for 2hours. The polarity was inverted at the end of an hour. The doped regions were removed in the KOH solution [Gautier, Ventura, Jérisian, Kouassi, Leborgne, Morillon & Roy (2006)].

In a recent study, Oubensaid, Duluard, Pichon, Morillon, Boufnichel, Lefaucheux, Dussart, & Ranson (2009) used the thermomigration process to produce aluminum-doped walls in n-type silicon. Thermomigrated regions were then removed using cryogenic etching to produce deep trenches. Several process characteristics such as the rate of the evolution of the trench depth were studied. A linear etching of the thermomigrated regions with a rate of 8 μm/min was observed. The trench sidewalls were vertical and the bottom was horizontal. There was however some undercut due to the etching of the region below the mask. This was attributed to the catalytic reaction of aluminum with silicon during etching. To remedy this, the standard cryogenic etching technique was replaced by the STiGer etching where it resulted in a significant reduction of the undercut. The STiGer process is a time-multiplexed cryogenic etching method designed to achieve high aspect ratio structures on silicon [Tillocher, Kafrouni, Ladroue, Lefaucheux, Boufnichel, Ranson & Dussart (2011)]. Using atomic electron microscopy, the roughness of the sidewall and bottom walls were estimated to be about 400 nm.

Schulze and Strack (2006) patented a thermomigration-based process in order to produce a buried metallic layer inside a semiconductor body. A semiconductor body is chosen, which comprises two layers forming the front and rear surfaces. The first layer is a highly n-doped or p-doped substrate depending on the application purpose. The second layer is applied to the first substrate by means of an epitaxial method, and is doped more weakly than the first semiconductor substrate. Depending on the application, the second semiconductor layer could be of the same conduction type as the first semiconductor layer or doped complementarily.

For the fabrication of a buried metallic layer in the semiconductor body, a metal layer such as aluminum is applied to one of the sides (rear side in Figure 10a). A positive temperature gradient is established such that the temperature increases proceeding from the rear side in the vertical direction. RTA method may be used to establish the temperature gradient. The migration process stops if the temperature in the region in which the metal is situated during the migration process is lowered to a temperature below the eutectic temperature. The initially liquid metal that has migrated into the semiconductor body then condenses to form a buried metallic layer in the semiconductor body (Figure 10b). The position of the metallic layer in the semiconductor body can be established by adjusting the temperature gradient. The metallic layer contains a mixture of semiconductor material and predominantly metal, which therefore has both a very good conductivity and a very strong recombination effect.

In the above mentioned patents, the method of producing the conductive channels was the subject of the patent, where RTP or other methods were used to establish a temperature gradient. In a patent by Kudella, Reetz, Enßlen, Rasel, Schindel, & Kriegel (2006), a device was invented to produce conductive channels by thermomigration. The device is vacuum-tight and is filled with a good heat conductive gas. An inductive heater is used as the heat source and a liquid-cooled coil is used as the heat sink.

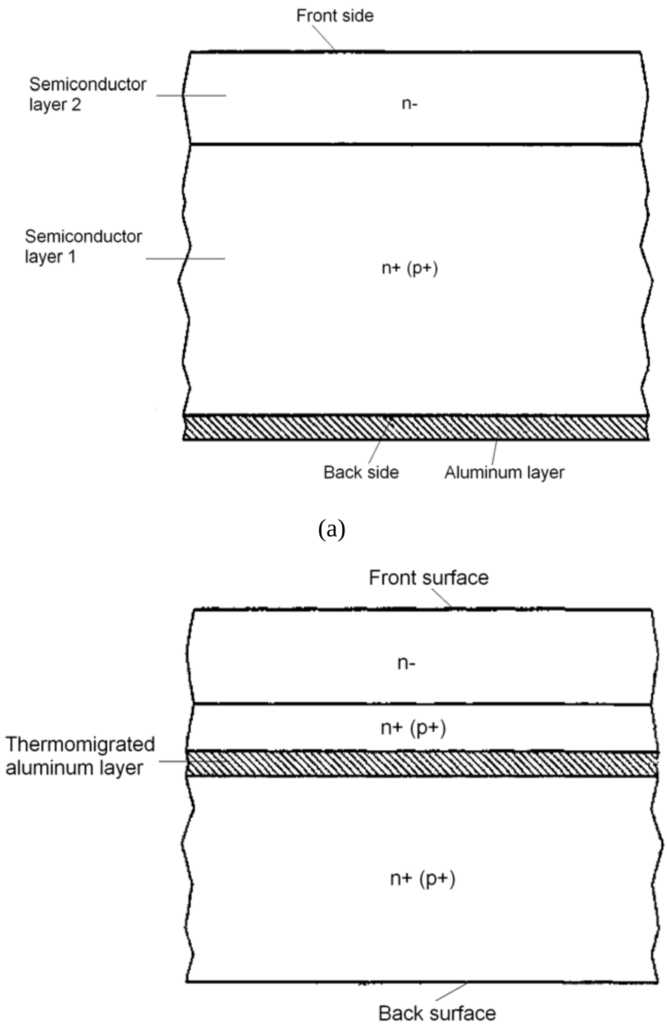


Figure 10: The formation of buried metallic layers within a semiconductor body; (a) before the start of thermomigration, and (b) after thermomigration.

5 Fabrication of Three-Dimensional Arrays in Semiconductors

Thermomigration has been also used to produce an array of silicon sharp needles or spikes that may be used for cortical penetration or as a neuron interface. Elongated electrodes are mounted to the base. The electrodes are electrically isolated from each other at the base by means of a second material positioned between the electrodes. Signal connection means is linked with the electrodes for providing electrical connection to each of the electrodes individually.

To form an array, pads of aluminum on a silicon substrate are thermomigrated through an n-type silicon block. This leaves behind trails of p-doped channels isolated from each other by opposing p-n junctions. A combination of mechanical and chemical techniques may be used to remove the regions between the thermomigrated columns and expose the needles. The needles need to be post-treated to create active electrode areas and contact pads [Campbell, Jones, Huber, (1991); Normann, Rousche, Horch, & Schmidt (1994)] (see Figure 11).

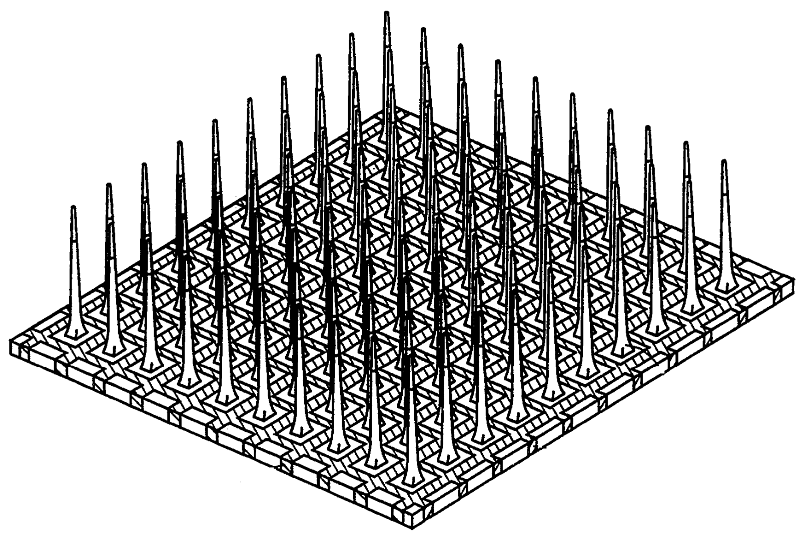


Figure 11: Three-dimensional array of p-type needles made by thermomigration of aluminum pads in a silicon block [Normann, Rousche, Horch, & Schmidt (1994)].

6 Fabrication of Solar Cells

Some materials such as semiconductors exhibit the photovoltaic effect that causes them to absorb photons of light and release electron-hole pairs. When light energy strikes the solar cell, electrons are knocked loose from the atoms in the semiconductor material. If the material is treated or doped properly to prevent electron-hole recombination, and electrical conductors are attached to the positive and negative sides, an electrical circuit is formed and the electrons can be captured in the form of an electric current.

Photovoltaic solar energy harvesting technologies can be divided into two camps: (a) crystalline silicon and similar technologies that are efficient but costly; (b) technologies that offer lower cost per unit area, but fail to deliver compelling efficiencies such as amorphous polymer and organic thin film solar cells. Below a threshold, cost of the solar energy will become competitive with legacy energy technologies, such as coal. The current trend is towards reaching that threshold and soon solar cells will be playing a more important role in our daily life.

In this section, the application of thermomigration in the fabrication of silicon solar cells is considered. This was apparently first introduced in a patent by Anthony, Cline & Winegar (1976). The invented solar cell comprised a body of semiconductor material having two parallel opposed major surfaces, one of the surfaces being exposed to radiation. The solar cell may be fabricated by thermomigration or its combination with epitaxial growth techniques.

The invented solar cell is composed of a doped semiconductor material having a selected resistivity and conductivity. The main semiconductor body is mechanically polished, chemically etched, rinsed and dried in air. An acid resistant mask such as silicon oxide is disposed on the surface of the body. Employing photolithographical techniques, a photoresist is disposed on the surface of the silicon oxide layer. A suitable mask of spaced lines of a predetermined thickness is disposed on the layer of photoresist. After exposure to ultraviolet light, the layer of photoresist is washed to open windows in the mask where the lines are desired so as to be able to selectively etch the silicon dioxide layer. A metal layer such as aluminum is deposited on remaining portions of the layer of silicon oxide and on the exposed silicon in the troughs, using a metal evaporation chamber. The metal in the troughs are the metal "wires" to be migrated through the body. The processed body is placed in a thermomigration apparatus where the metal wires in the troughs are migrated through the body. A thermal gradient of approximately 50˚C per centimeter between the bottom (hot) surface and top (cold) surface was suggested for an average temperature of the body from 700˚C to 1350˚C. In this process, each region below the original wires is heavily p-doped and has low resistance, which is desirable for solar cells. Additionally, the body is divided into a plurality of spaced non-doped regions having the same conductivity as the body. A p-n junction is formed by the contiguous surfaces of each pair of mutually adjacent regions of opposite type conductivity. The p-n junction, as formed, is very abrupt and distinct resulting in a stepped junction.

Figure 12 shows the patented solar cell by Anthony, Cline & Winegar (1976). When radiation impinges upon the upper surface of the solar cell and penetrates into the plurality of doped and un-doped regions, photons are absorbed in the structure of the solar cell causing the formation of electron-hole pairs produced anywhere within the body. These pairs will have only a short distance to diffuse to be collected by a p-n junction. The short diffusion distance to a p-n junction is due to each doped and un-doped region being less than one diffusion length.

Electrical contacts for collecting the carriers which are collected by the p-n junction are kept clear of the top surface. As displayed in Figure 12, a typical electrical contact arrangement for the solar cell of this invention is shown disposed on the surface. The contacts effectively connect the plurality of p-n junctions into one p-n junction. A layer of an electrical insulating material permits bridging of similar regions. Electrical leads are affixed to opposite contacts for electrically connecting the solar cell to the electrical circuitry external to the cell.

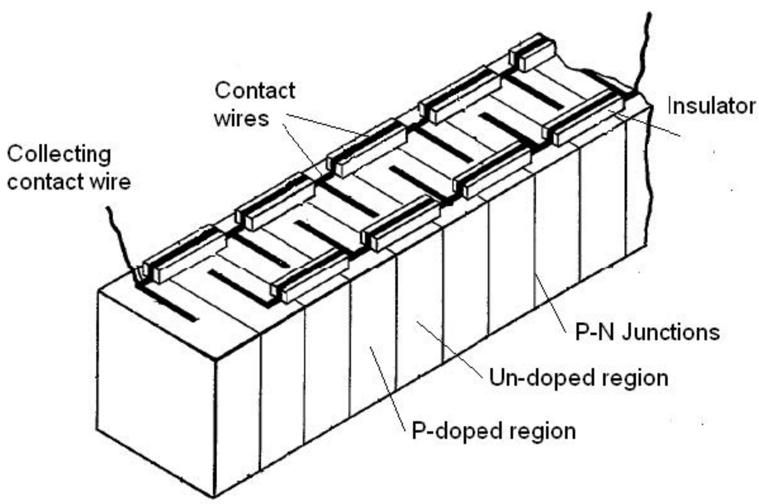


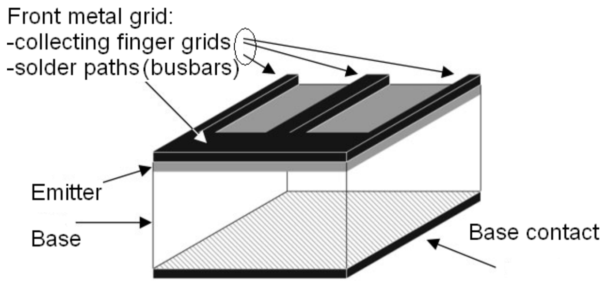
Figure 12: Fabrication of a semiconductor solar cell using thermomigration [Anthony, Cline & Winegar (1976)].

Norskog and Warner, Jr. (1981) later argued that the above described invention may suffer from low bulk lifetime as the thermomigrated regions of the device must function as active regions. Also, the edge illumination in the cell may cause a current recirculation and consequently loss of power. They proposed an alternative arrangement wherein the thickness of the p-doped region is much less than that of the original n-typed semiconductor. In this arrangement, the p-type thermomigrated region does not actively participate in the harvesting process.

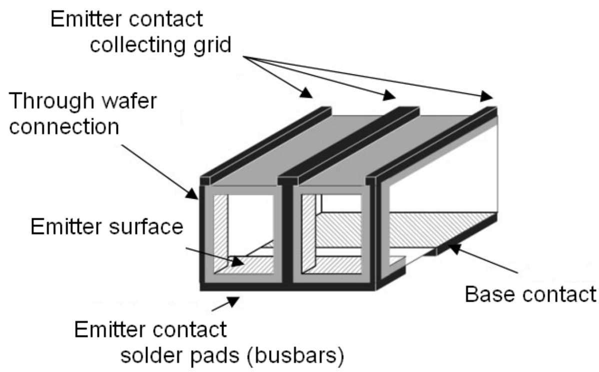
In the above mentioned inventions [Anthony, Cline & Winegar (1976); Norskog and Warner, Jr. (1981)], thermomigration had been used to fabricate p-n junctions in a conventional silicon solar cell. Back-contact cell is an alternative to cells with front and rear contacts, in that both the positive and negative external contacts are positioned on the rear surface. In the last decade, interest in back-contact cells has been growing and a gradual introduction to industrial applications is emerging [Van Kerschaver & Beaucarne (2006)]. A schematic representation of a conventional crystalline silicon solar cell is shown in Figure 13a. The silicon base is the main part of the mechanical structure. Solar cells that use inexpensive silicon substrates contain greater amounts of impurities and crystalline defects, which limit the internal collection depth of photo-generated carriers. Therefore such cells generally have a carrier-collection junction (i.e., "emitter layer") on the front surface, where most of the light is absorbed, in order to obtain a high collection efficiency of photo-generated carriers. For silicon solar cells, the bulk silicon substrate is generally doped p-type and the emitter layer is generally a thin, heavily-doped, n^+ layer that is formed in an emitter diffusion step by solid-state diffusion of phosphorus at elevated temperatures. The emitter is located near the top or front surface. A metal grid to extract the carrier from the device contacts each of these silicon regions. Whereas the rear surface is often fully covered, on the front surface the metal grid is the result of a trade-off between having low coverage to limit optical losses and high coverage to limit resistive losses. Most manufactures apply a front grid consisting of thin parallel lines (fingers) that transport the current to centrally located bus-bars.

In a contact wrap-through back-contact cell, which is most closely linked to the conventional cell structure, the emitter is located near the front surface, but part of the front metallisation grid is moved from the front to the rear surface. In the schematic representation in Figure 13b, this is depicted as the bus-bar moving from one surface to the other. The remaining front surface grid is connected to the interconnection pads on the rear surface by extending it through a number of openings or holes in the wafer. Back-contact cells have higher conversion efficiency due to reduced contact-obscuration losses. Also assembly of back-contact cells into electrical circuits is easier and cheaper because both polarity contacts are on the same surface. Better aesthetics by providing a more uniform appearance, which is important in building-integrated photovoltaic systems, is another advantage.

An important issue for back-contact silicon solar cells is identifying a cell design and a fabrication process that is inexpensive to manufacture and that can use inexpensive, lower-quality silicon substrates. Back-contact solar cells usually use an array of laser-drilled holes to effectively wrap the emitter layer from the front surface around to the back surface (therefore called Emitter-Wrap-Through (EWT) back-contact solar cells). Designs that use laser-drilled holes to make conductive



(a)



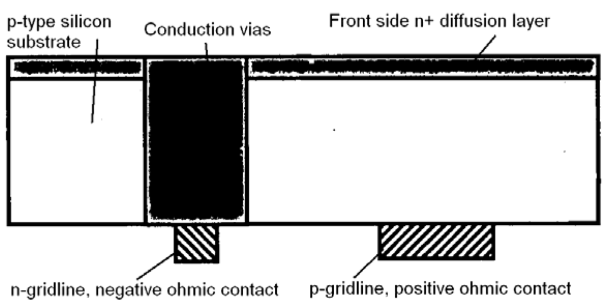
(b)

Figure 13: A schematic of a conventional silicon solar cell (a) and a back-contact solar cell (b) [Van Kerschaver & Beaucarne (2006)].

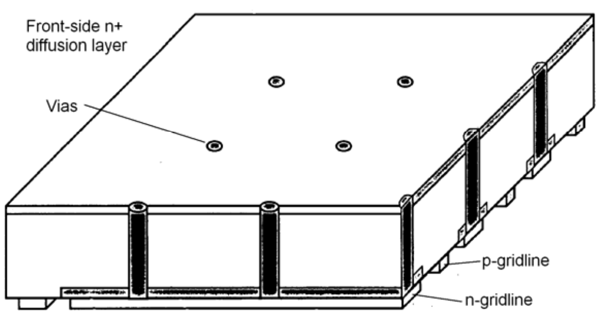
vias have several disadvantages such as the need for drilling a large number of holes, loss of structural integrity, and the added cost and manufacturing time. Additionally, the conductivity of the laser-drilled vias is limited by the achievable concentration of n-type dopant, and by the depth of the emitter diffusion layer realized on the interior surfaces of the laser-drilled holes.

In an attempt to provide a better means to fabricate the back-contact cells, Gee and Smith (2006) and (2007) explain a method using thermomigration to fabricate conductive channels (vias) of heavily doped silicon. Closely-spaced n^{++} conductive vias electrically connect an n^{+} emitter layer on the front surface of a solar cell to ohmic contacts located on the cell's back side. Multiple vias can be fabricated simultaneously.

Schematic diagram of the side view and the perspective view of a thermomigration treated back-contact solar cell is shown in Figure 14 [Gee and Smith (2006) and (2007)]. The cell comprises a p-type bulk silicon substrate, an n^+ diffusion emitter layer located on the front side of the substrate, an n^+ diffusion emitter layer located on the back side of the substrate, an n-gridline negative ohmic contact located on the back side, contacting back side emitter layer, an n^{++} conductive via disposed through the thickness of the substrate that electrically connects front side emitter layer to negative ohmic contact located on the back side and a p-gridline positive ohmic contact located on the back side that is electrically connected to the p-type silicon substrate. Conductive vias also contact back side emitter layer. In Figure 14b, a closely spaced array of conductive vias is seen. The spacing can be from 1-2 mm and the diameter can be from 25-150 microns. The n-gridlines and p-gridlines are interdigitated on back side and optimized to minimize electrical resistance and carrier recombination. P-bus-bar connects individual p-gridlines.



(a)



(b)

Figure 14: Schematic diagram of the side view (a) and perspective view (b) of a back-contacted solar cell with conductive vias, patented by Gee and Schmit (2006) and (2007).

The fabrication process has several steps: a thin, p-type bulk silicon substrate is cleaned and etched. A patterned diffusion barrier is created to mask off a portion of the back side of the substrate. Then, a phosphorous diffusion step is performed, which creates a front side n^+ emitter layer and a back side n^+ emitter layer. The presence of diffusion barrier prevents the underlying area of the substrate from being doped with phosphorus. Diffusion barrier is removed by performing a hydrofluoric acid etch. This exposes an un-doped area of p-type silicon substrate that subsequently will be covered with an ohmic contact gridline. Metal carrier droplet of an n-type dopant material is deposited on top of the front side n^+ emitter layer. An array of closely-spaced droplets may be simultaneously deposited. RTP is used to create a temperature gradient through the substrate's thickness. The recrystallized cylindrical zone that forms after the passage of droplet comprises a sufficiently high residual concentration of n^{++} dopant left behind in droplet's trail to make vias electrically conductive with respect to n-type emitter layers, while also being electrically insulating with respect to p-type bulk silicon substrate. By penetrating through back side emitter layer, n^{++} doped conductive via electrically connects the front side emitter layer to the back side emitter layer. N-gridline negative and p-gridline positive ohmic contacts are the final parts to be fabricated.

Recently, Schmit and Gee (2010) patented a modified version of the above mentioned back-contact solar cell. The objective of the new version is to overcome the prior limitations on the thickness of the crystalline wafer. The energy conversion efficiency is higher with the EWT cell structure utilizing the thinner crystalline silicon wafers because there is no shadowing of the incoming light by electrical contacts on the front side. The light has a completely unobstructed path into the solar cell. In addition, the energy conversion efficiency is higher with the EWT cell structure on thin wafers because there is some electrical current generation at the back surface as well as the front surface. Thus the amount of raw material per cell is significantly reduced and the energy conversion efficiency is increased.

The process for fabricating the back-contact EWT cells is chosen and designed such that the light will not pass through the wafer, even at very low thicknesses, but without any requirement for an aluminum back layer as found in a conventional solar cell. The application of the EWT on thin wafers reduces the raw material consumption, and therefore cost, and also improves the performance in comparison with the conventional solar cells. This higher performance is a direct result of the synergistic combination of thin wafers and an EWT design. Efficiencies of about 15-17% have been claimed for this back-contact EWT design [Schmit and Gee (2010)].

EWT cells have numerous holes in the wafer, which are typically drilled with a laser, or have passages formed by other methods such as thermomigration. By using thin wafers the processing time is reduced. Also vias connect the front surface of the substrate to the back surface of the substrate which may be formed by laser drilling, dry etching, wet etching, mechanical drilling, and water jet machining, preferably followed with a diffusion of a dopant into the walls of the holes to make a conductive via. Alternatively the vias comprise a substantially solid cross section and comprise doped substrate material and are formed by thermomigration.

7 Material Property Manipulation in MEMS and NEMS Devices

In this section, one new emerging application of thermodiffusion in micro- and nano-electronic devices is introduced: changing the materials properties in a particular application using thermomigration, in this case the fabrication of silicon micromechanical resonators.

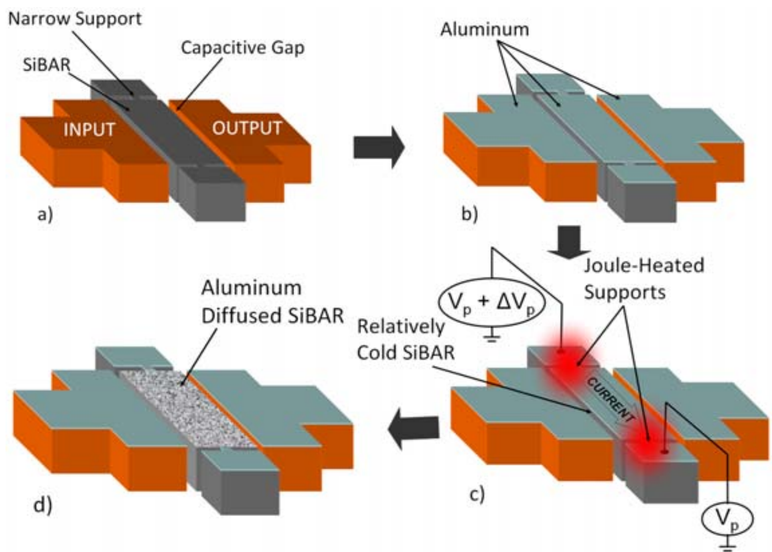


Figure 15: Schematic diagram of aluminum thermomigration into silicon bulk acoustic resonators (SiBAR) for temperature coefficient of frequency (TCF) reduction [Samarao & Ayazi, (2009)].

The application of integrated devices is a good alternative to discrete frequency-selective devices in MEMS and NEMS applications. An example is the silicon micromechanical resonators that can enable a cost-effective integrated platform for timing, wireless connectivity and multi-band spectral processing. However, there is one problem involved: the uncompensated temperature coefficient of frequency (TCF) for a native silicon resonator is far greater than that of quartz resonators.

To achieve stable low-phase-noise frequency references in silicon micromechanical resonators, the TCF of silicon may be compensated without compromising on the quality factor of the resonator, using doping through changing the number of free charge carries in a silicon wafer, using thermodiffusion of aluminum into silicon [Samarao & Ayazi, (2009)]. The uniformity and speed of aluminum thermomigration is enhanced by the presence of boron atoms in silicon. This has been investigated by evaporating a thin layer of aluminum onto the silicon bar acoustic resonators (SiBAR) (Figure 15(b)) and joule-heating it by passing a current through the SiBAR element via the narrow support elements (Figure 15(c)) [Samarao & Ayazi, (2009); Samarao, Casinovi, & Ayazi (2010)]. Aluminum diffuses through the silicon towards the hot support elements thereby doping it (Figure 15(d)). Their results show that the TCF of silicon bulk acoustic resonators are reduced from -29 ppm/°C to -2.72 ppm/°C on 20 μm thick devices using boron-assisted aluminum thermomigration in silicon, while maintaining a high quality factor of 28000 in vacuum.

8 Summary and Conclusions

Some of the applications of thermomigration or temperature gradient zone melting method in the fabrication of semiconductor-based devices were described. These applications in MEMS and NEMS devices include the formation of p-n junctions in electronic devices, the formation of conductive vias and also empty channels and trenches in a semiconductor body, preparation of three-dimensional arrays such as an array of sharp silicon needles for cortical penetration, and altering silicon material properties through doping by thermomigration. Application of thermomigration in an emerging energy source, namely solar cells was also investigated. Thermomigration may be used to fabricate conventional and back-contact silicon solar cells. Recent advances in the form of research papers or patents were described.

Although thermodiffusion or thermomigration in semiconductors and metal mixtures has not been adequately explored from a theoretical point of view, this review shows its strong potential in the synthesis of advanced materials and devices such as the state-of-the-art MEMS, NEMS, sensors and solar cells. Better theoretical understanding of the process and further experimental work on the effect of processing parameters will lead to more effective implication of the method in advanced materials synthesis.

While some of the applications of thermomigration in semiconductors date back to decades ago such as in the fabrication of silicon solar cells, thermomigration also has been used in recent developments such as in the fabrication of frequency-selective devices. In other words, its applications are not limited to those discovered so far and considered here and future applications are expected. Therefore, even though it is still a research topic and not considered as a commercialized technique yet, its positive characteristics such as the controllability through adjusting the temperature gradient in the wafer, suitability for a variety of applications, and not altering the integrity of the main body of the device are the positive characteristics of the technique.

The modeling of the process, i.e. thermodiffusion in molten metal-semiconductor mixtures is still challenging. This is partly because of the complexity of thermodiffusion in liquid mixtures itself, and also the presence of instabilities, convection and other complexities in metal-semiconductor mixtures, in particular.

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