Method for Thermally Treating Semiconductor Wafers

The present invention relates to a method for thermally treating semiconductor wafers in a reaction chamber.

Thermal treatment, in addition to the controlled temperature variation for the technical processing of a semiconductor substrate, is also understood to mean all further processes that occur in the course of this treatment, such as, for example, chemical reactions, structural changes, or other changes in physical characteristics of the semiconductor substrate that is being treated.

A method for thermally treating semiconductor substrates is disclosed, for example, in US Patent Nr. 5,935,650. With this method, a semiconductor substrate that is to be treated is rapidly heated to a prescribed temperature, while the substrate is held in a prescribed gas atmosphere. When the prescribed temperature is reached, the substrate is held at this temperature for a fixed period of time, and is subsequently rapidly cooled off to a lower temperature, at which it is held. While the substrate is held at this lower temperature, an exchange of the gas atmosphere takes place, and the substrate is subsequently rapidly heated within this new atmosphere to a prescribed further temperature, is held at this temperature for a fixed

period of time, and is subsequently again cooled off. This specialized manner of proceeding with two successive heatings of the substrate in different gas atmospheres is utilized in order to form thin oxide layers upon the semiconductor substrate.

DE-A-199 20 871.9, which belongs to the same applicant and is not pre-published, furthermore describes thermally treating semiconductor substrates, such as, for example, a GaN III-V semiconductor. With these semiconductors there results the problem that, for example in a surface layer doped with magnesium, the magnesium acceptors are passivated by hydrogen and are thus electrically inactive. To overcome this electrical inactivity, the magnesium-hydrogen bonds must be broken up, and the then unbound hydrogen must be diffused out of the semiconductor crystal in order to achieve a good p-conductivity of the doped layer. These bonds are conventionally broken by thermally treating the material. With the aforementioned GaN, which is doped with magnesium, the magnesium-hydrogen bonds break up approximately at temperatures over 400°C. At these temperatures, however, the hydrogen has a short diffusion length and thus hardly diffuses out of the GaN crystal. At higher temperatures, the diffusion length increases in the semiconductor crystal. However, at these temperatures the semiconductor crystal begins to dissociate, so

that the temperature of the substrate cannot be increased to any desired level. With GaN, for example, nitrogen is released from the crystal, so that blank sections or vacancies result that counteract the desired p-conductivity of the crystal.

Thus, with the thermal treatment of substrates at high temperatures, two opposing processes occur that become more pronounced as the temperature of the crystal increases, whereby on the one hand the p-conductivity increases, while on the other hand it is inhibited.

In this connection, it is noted that the diffusion effect of the hydrogen forms more rapidly than the dissociation of the crystal sets in, so that with the method described in the aforementioned DE-A-199 20 871, despite the undesired dissociation process, the semiconductor crystal is briefly heated via a special temperature curve to a very high temperature in order to promote the diffusing-out of hydrogen and to thus achieve an improved p-conductivity.

In addition to the fact that temperatures at or above the thermal dissociation temperature of semiconductor materials can be damaging, it is important to also keep the overall thermal stress of the semiconductor material to a minimum.

US-A-4,201,559 discloses a method for producing a glass-ceramic, according to which a thin glass body, such as a glass fiber, is converted into a glass-ceramic body by thermal treatment. The thermal treatment comprises a plurality of heating and cooling cycles, whereby the heating is effected via a split laser beam.

DD-A-226 437 shows a method for producing highly-oriented structures in halogenated vinyl polymers by an alternating heating of a polymer body in an electrical field.

Proceeding from the aforementioned documents, it is an object of the present invention to provide a simple method that enables an effective treatment of semiconductor substrates and reduces the thermal stress thereof.

Pursuant to the present invention, this object is realized with a method of the aforementioned type in that the treatment includes the heating-up of at least portions of the semiconductor substrate to at least three temperature peaks having appropriate cooling phases therebetween. In so doing, the desired treatment result is promoted and accelerated by alternating high and low temperatures. This acceleration makes it

possible to minimize the overall thermal stressing of the semiconductor substrate. In particular with semiconductor materials of the aforementioned type, the diffusing-out of hydrogen is promoted and thus an improved p-conductivity is achieved. Since the diffusion effect of the hydrogen is increased more rapidly at high temperatures than does the dissociation of the crystal set in, with the above method the desired diffusion effect is promoted while the non-desired dissociation is not permitted or is permitted to only a slight extent.

Pursuant to a particularly preferred embodiment of the invention, the temperature variation has a frequency modulation, an amplitude modulation and/or a keying ratio modulation in order to optimally adapt the thermal treatment and to achieve the desired result. For example, first a very high temperature peak can be established in order to rapidly initiate the desired process, while the successive temperature peaks have a lower amplitude in order to maintain the desired process.

In order to control the result of the thermal treatment, a process atmosphere that is found in the reaction chamber and surrounds the semiconductor substrate is preferably varied. In so doing, in particular the composition and/or the pressure of a fluid in the reaction chamber is varied in order to optimize the desired effect. The variation of the

process atmosphere preferably has a frequency modulation, an amplitude modulation and/or a keying modulation. In so doing, the process atmosphere is preferably essentially kept constant for a time interval that includes at least two successive temperature peaks in order to achieve constant treatment effects.

At least at one point in time during the thermal treatment the process atmosphere preferably has an underpressure in order to promote a diffusing-out of elements from the semiconductor substrate and to reduce the diffusing-in of impurities. However, an overpressure of the process gas atmosphere can also be advantageous, whereby the partial pressure of the substance in the process gas atmosphere that is diffusing out is as low as possible. As a result, for example the dissociation rate of the substrate can be considerably reduced at a prescribed temperature. One example is GaN:Mg, which is produced in a N_2 atmosphere with overpressure, whereby the H_2 fraction in the process gas atmosphere is as low as possible.

For a good control of the process, the temperature change and the change of the process atmosphere have a controlled phase relationship, in particular a shifting. In so doing, the phase shift can be

as desired, i.e. between 0 and 2π. For a flexible process control, the phase shifting is modulated during the treatment.

Pursuant to one preferred embodiment, the temperature change is effected by electromagnetic radiation, since this enables rapid and easily controllable temperature changes, especially of portions of a semiconductor substrate, such as, for example, only a surface region. In addition or alternatively thereto, the temperature is effected by contact with a fluid and/or a fixed body. In particular during the cooling-off phases, the temperature changes can be accelerated by contact with a fluid, such as, for example, an inert gas. In so doing, preferably at least one surface layer, especially a doped surface layer of the substrate, is heated in order to achieve alterations of this layer, such as, for example, the diffusing-out of one element or a phase conversion. Pursuant to one embodiment of the invention, the temperature of at least one temperature peak is greater than the dissociation temperature of the substrate in order to rapidly initiate the desired effect. In this connection, the temperature peaks are preferably kept so brief that essentially no dissociation of the crystal structure of the substrate occurs.

The length of the temperature peaks is preferably between 0 and 10 seconds in order to minimize the thermal stressing of the semiconductor substrates. In order to achieve good treatment results with semiconductor substrates, at least one temperature peak is between 750 and 1050°C. At these temperatures, for example the aforementioned magnesium-hydrogen bonds are completely broken up and the diffusion lengths of the hydrogen atoms are significantly increased in order to promote and to accelerate a diffusing-out of the hydrogen from the doped surface layer of a semiconductor material. The temperature between two temperature peaks is preferably cooled to 300 to 600°C, which is adequate to suppress a dissociation of, for example, a semiconductor wafer, and at the same time the processes that have been initiated, such as, for example, the diffusing-out of hydrogen, are maintained.

To promote the treatment, the semiconductor substrate is preferably subjected to UV radiation. It is, however, also advantageous to subject the semiconductor substrate to a magnetic and/or electrical field. Furthermore, the intensities and/or field strengths are modulated pursuant to a further embodiment.

The invention will subsequently be explained in greater detail with the aid of preferred embodiments with reference to the figures.

Shown are:

Figures 1A to C	graphs of temperature curves plotted pursuant to the present invention;
Figure 2	a graph of a further temperature curve pursuant to the present invention, especially for processing GaNMG semiconductor substrates;
Figure 3	a plot that shows the dependency of the diffusion length of H^+ in p-GaN as a function of the number of temperature peaks;
Figure 4	a graph that shows the dependency of the conductivity of p-type GaN as a function of the number of temperature peaks; and
Figure 5	a graph that shows a further temperature curve pursuant to the present invention.

The Figures 1A to 1C show graphs of temperature curves pursuant to the present invention. The temperature T is plotted as a function of the time t. The illustrated graphs show, in idealized form, the temperature

curve of the treated objects, especially semiconductor wafers. The wafers are heated cyclically several times to an increased temperature T_1 within a reaction chamber and a prescribed process atmosphere, and are subsequently cooled off to a lower temperature T_2. With the graphs shown in Figures 1A to C, the temperature curve essentially describes a box shape, whereby the lengths of the peaks at the temperature T_1, as well as the lengths of the peaks at the temperature T_2, have the same length. There thus results for the curve a keying ratio of approximately 1. The spacing between the temperature peaks, as well as the height of the temperature peaks and of the temperature minima, are constant over the entire cycle. Although the temperature peaks and temperature minima, the keying ratio, as well as the spacing between the temperature peaks is illustrated as being uniform in Figures 1A to C, it should be noted that the shape of the curve can be controlled in any desired manner, especially during the heating phase, for example, it can be parabolic, and that all of the aforementioned parameters can be modulated, especially also the shape of the curve, in order to optimally adapt the process conditions to the object that is being treated.

As shown in Figure 1A, during the first two cycles the process atmosphere that surrounds the object is kept constant, whereas during

the following cycles atmospheric changes are possible. Pursuant to Figures 1B and 1C, a constant process atmosphere is maintained with two middle cycles (Figure 1B) or the last two cycles (Figure 1C) respectively of the thermal treatment. It is, of course, also possible to provide a constant process atmosphere over a plurality of cycles in order to provide a constant treatment during these cycles.

Figure 2 shows a temperature curve for the thermal treatment of a GaN:Mg-semiconductor substrate. After doping of the substrate, the magnesium acceptors are first passivated by hydrogen and are thus electrically inactive. It is therefore necessary to break up the magnesium hydrogen bonds, and to diffuse the hydrogen out of the substrate so that the material achieves a desired p-conductivity.

As can be recognized in Figure 2, the temperature of the doped surface of the substrate, starting from a temperature of about 220°C, is rapidly heated to a temperature of about 500°C. The substrate is held at this temperature for about 10 to 20 seconds in order to achieve a homogeneous temperature distribution over the entire substrate. The magnesium-hydrogen bonds begin to break up at these temperatures, although the hydrogen at this temperature has a relatively low diffusion length, so that very little hydrogen diffuses out of the substrate. After

this temperature stabilization, the substrate, or at least the surface layer of the substrate, is rapidly heated to about 950°C, and is subsequently immediately cooled off essentially without any delay. The temperature of 950°C is close to the dissociation temperature of the GaN substrate if the process gas pressure corresponds to one bar and N_2 is used as the process gas. At this temperature, nitrogen begins to be freed from the crystal structure or composite of the substrate, as a result of which blank sections or vacancies can occur that counteract a desired p-conductivity of the substrate. This dissociation process is, however, very slow, and since immediately after reaching this temperature the substrate is again cooled off, there essentially results no dissociation of the substrate. The desired diffusion effect, i.e. an increased diffusion length of the hydrogen, in contrast forms more quickly, so that due to the short temperature peak a significantly improved diffusion effect results for the hydrogen.

After the temperature peak is achieved, the substrate is cooled to a temperature between 400 and 450°C, i.e. to a range in which magnesium-hydrogen bonds are still broken up, and diffusion of the hydrogen takes place. After the prescribed temperature minimum is achieved, the substrate is again rapidly heated, and in particular to a temperature over 800°C, and is subsequently again rapidly cooled off.

This alternating rapid heating to a temperature of over 800°C, and cooling to a temperature between 400 and 450°C, is repeated a number of times, so that on the whole 9 temperature peaks are produced that are just over 800°C. On the whole, thus 10 temperature peaks are produced.

During this thermal treatment, the GaN substrate was in an essentially constant N_2 atmosphere at normal pressure. Alternatively, however, the pressure of the atmosphere in the process chamber can also be altered, so that, for example, an overpressure or an underpressure up to $5x10^{-3}$ millibar or less can be applied to the process chamber, whereby, as previously mentioned, due to an overpressure the dissociation rate of the GaN is reduced, for which reason the substrate can be heated to higher temperatures, which in turn enhance the diffusing-out of the hydrogen.

Figure 3 illustrates the results of plotting the diffusion length of hydrogen against the number of temperature peaks with a p-GaN substrate. In this connection, the plotting or evaluation provides a temperature curve as illustrated in Figure 2. The diffusion lengths were determined pursuant to the teachings of S. J. Pearton for the diffusion constant under the arbitrary assumption of a diffusion time of 0.1

second. As can be recognized in Figure 3, the diffusion length increases with the number of temperature peaks. Thus, with a doped surface layer of 1μm, six heatings would be sufficient in order, from a statistical viewpoint, to diffuse out essentially all of the hydrogen ions found in a layer onto the crystal surface.

This result is also supported by the measurement values that are illustrated in Figure 4 and that illustrate the measured conductivity of p-GaN as a function of the number of temperature spikes or peaks. As can be seen, the measured conductivity increases as the number of temperature peaks increases. This is due to the fact that the temperature peaks effectively increase the diffusion length of the hydrogen, as a result of which more hydrogen diffuses out of the substrate and leaves behind activated Mg acceptors. Due to the brief temperature peaks, a dissociation of the crystalline substrate structure that would adversely affect the p-conductivity of the substrate does not occur, or occurs only to a slight extent. Due to the temperature control described above, an excellent p-conductivity of Mg-doped GaN substrates can thus be achieved.

Deviating from the above-illustrated temperature curve, the temperature of the object can be modulated with respect to frequency,

amplitude, or keying ratio, whereby it is not necessary for the entire substrate to follow the controlled temperature change. In certain applications it can be sufficient that merely portions of the substrate, especially the uppermost layers, on which components or structures are disposed, follow the temperature curve. In general, it is also possible to modulate the frequency, the amplitude, the keying ratio of the process gas pressure or the composition of the process atmosphere. The phase relationship of the temperature curve, as well as the variation of the process atmosphere, can be controlled. Furthermore, individual types of modulation can be combined with one another in any desired manner, for example by carrying out two or more temperature modulations and/or two or more pressure modulations.

In addition to the aforementioned embodiment, the invention can also be advantageously used with the thermal treatment of silicides, for example with phase conversions of, for example, $TiSi_2$ from the C49 into the C54 phase, which has a considerably greater conductivity.

It has been shown that, for example, the C49-C54 phase conversion temperature increases with small structure sizes or small layer thicknesses of the silicide layer. For example, the phase conversion

temperature increases from about 720°C to about 770°C if the layer thickness is reduced from 60 nanometers to 25 nanometers. This increases the thermal stress of the wafer in a disadvantageous manner. As a consequence of an extremely rapid heating-up, the phase conversion temperature can again be reduced somewhat. However, in order to achieve as complete a phase conversion as possible, a plurality of successively following temperature peaks are utilized, as illustrated for example in Figure 1. In this connection, the temperature peaks should be approximately 750°C to 1000°C, and temperature minima should be about 300°C to 600°C. These temperature ranges are also applicable for the previously described embodiment. The heating-up rates are greater than 150°C per second, and the cooling-off rates are about 60°C per second to 150°C per second. The time during which the wafer is held at the temperature T_1 is preferably in the range of between one second and about 10 seconds, whereby, however, shorter or longer times are also possible. In contrast, the duration at which the temperature curve is at a minimum is preferably reduced to 0 seconds, so that a temperature curve results as is illustrated in Figure 5.

In order to promote the respective process during the thermal treatment, it is possible to irradiate the substrate or wafer that is to be

handled with UV light, and/or to expose the substrate to a magnetic field or an electrical field. In so doing, the UV intensity and/or the strength of the magnetic field or the electrical field can advantageously additionally be modulated in conformity with the aforementioned types of modulation. In so doing, the direction of the lines of flux relative to the wafer can follow any predefined direction, which itself can then again be varied with respect to time.

Furthermore, the applications of the aforementioned fields and the UV radiation are not limited to such applications where the wafer is subjected to a temperature modulation. Rather, the applications can also be used with processes where the wafer is processed with any suitable temperature-time curves.

In conjunction with the previously described method, it is in particular also possible or advantageous to vary the spatial arrangement of the elements that influence the temperature distribution relative to the object or substrate and/or to the process chamber. In order to this extent to avoid repetition, reference is made to DE-A 199..... which is from the same applicant and has the same filing date, and has the title "Method and Apparatus for the Thermal Treatment of Substrates".

Patent Claims

1. Method of thermally treating semiconductor substrates in a reaction chamber, characterized in that the treatment includes the heating-up of at least portions of the semiconductor substrate object to at least three temperature peaks with appropriate cooling phases therebetween.

2. Method according to claim 1, characterized in that the temperature change includes a frequency modulation, an amplitude modulation and/or a keying ratio modulation.

3. Method according to claim 1 or 2, characterized in that the process atmosphere in the reaction chamber is altered.

4. Method according to claim 3, characterized in that the composition and/or the pressure of a fluid in the reaction chamber is altered.

5. Method according to claim 3 or 4, characterized in that the alteration of the process atmosphere includes a frequency

modulation, an amplitude modulation and/or a keying ratio modulation.

6. Method according to one of the claims 3 to 5, characterized in that the process atmosphere is essentially kept constant for a time interval that includes at least two successive temperature peaks.

7. Method according to one of the claims 3 to 6, characterized in that the process atmosphere is provided with an underpressure at least to a point in time of the thermal treatment.

8. Method according to one of the preceding claims, characterized in that for the temperature curve and for the variation of the process atmosphere, a specific phase relationship, in particular a shifting, is provided.

9. Method according to claim 8, characterized in that the phase shifting is between 0 and 2π.

10. Method according to claim 8 or 9, characterized in that the phase shifting is modulated.

11. Method according to one of the preceding claims, characterized in that the temperature alteration is effected by electromagnetic radiation.

12. Method according to one of the preceding claims, characterized in that the temperature alteration is effected by contact of the semiconductor substrate with a fluid and/or with a fixed body.

13. Method according to claim 12, characterized in that at least a surface layer, especially a doped surface layer, of the semiconductor substrate is heated up.

14. Method according to one of the claims 12 or 13, characterized in that the temperature of at least one temperature peak is above the dissociation temperature of crystal structures of the semiconductor substrate.

15. Method according to one of the claims 12 to 14, characterized in that the temperature peak is so brief that essentially no dissociation of the crystal structure of the semiconductor wafer is effected.

16. Method according to one of the preceding claims, characterized in that the length of the temperature peaks in terms of time is between 0 and 10 seconds.

17. Method according to one of the preceding claims, characterized in that at least one temperature peak is between 750 and 1050°C.

18. Method according to claim 17, characterized in that the temperature between at least two temperature peaks is cooled to 300 to 600°C.

19. Method according to one of the preceding claims, characterized in that the semiconductor substrate is irradiated with UV light.

20. Method according to one of the preceding claims, characterized in that the semiconductor substrate is subjected to a magnetic field and/or an electrical field.

21. Method according to claim 19, characterized in that the intensity is modulated.

22. Method according to claim 20, characterized in that the magnetic field strength or the field strength of the electrical field is modulated.