A thermal control system e.g. for a PECVD (Plasma Enhanced Chemical Vapour Deposition) system comprising an energy source and a gas delivery system (fig. 3) including gas ratio control means for introducing a gas mixture between a substrate and a substrate holder 105 to control thermal coupling. A radiation detector e.g. a pyrometer (111, fig. 1) for measuring radiation emitted from a layer deposited on a silicon substrate is located on the opposite side of the substrate holder 105 to the substrate. The silicon substrate is at a temperature such that it is transparent at a selected frequency of electromagnetic radiation. A second electrode (123, fig. 4a) comprising openings e.g. a molybdenum mesh is located between a first electrode (the substrate holder 105) and a heat source e.g. UV, IR or optical lamps 116. The size of the openings may depend on the power supply frequency. Gas feed tube 120b is in thermal contact with heat source 116 to pre-heat process gases. A metal catalyst (703, fig. 7) is heated on the substrate in oxygen to provide a controlled oxide layer around metal islands before preparing carbon nanotubes in the PECVD system.
Figure 5

Figure 6
Figure 11
The following terms are registered trademarks and should be read as such wherever they occur in this document:

SEMI
Nanomaterials Growth System and Method

BACKGROUND

Technical Field of the Invention

The invention relates to the processing of substrates, that are at present used in the semiconductor industry, and in a preferred embodiment to the control of energy, which is electromagnetic in nature, and embodied as thermal energy within the substrate during processing. The invention also relates to processing a substrate that may have a pre-treated active layer including for example CMOS devices, and in an embodiment measuring the bulk temperature of the substrate, particularly close to the active layer, where control of the maximum temperature of the substrate is paramount to prevent damage to the active layer. The invention also relates to a PECVD system for growing nanostructures and in an embodiment carbon nanotubes on a substrate at CMOS process compatible temperatures, where the electrodes of the PECVD system can be optimised. The invention also relates to electrodes for a PECVD system.

Description of Related Art

In the semiconductor processing industry a variety of techniques are used to deposit films or nanostructures onto substrates or to modify materials already deposited on the substrate. Similar techniques can also be used in many other manufacturing processing industries. Such techniques are used in the production of, for example microelectronic devices, and include chemical vapour deposition (CVD) where a substrate is exposed to one or more volatile precursors which react or decompose on the surface of the substrate to produce the desired deposit. The activity of the precursors can be enhanced and controlled via the coupling of suitable energy processes to these elements. Other techniques include plasma enhanced chemical vapour deposition (PECVD) where the substrate is placed in contact with one of two electrodes and a plasma struck between the electrodes; the reaction rates and species of the precursors are enhanced by the plasma. Other techniques include reactive ion etching (RIE) where a plasma is used to remove material deposited on a substrate, and rapid thermal processing (RTP) where substrates are heated to high temperatures (e.g. 1200 °C) in a short space of time (a few seconds) and cooled in a
controlled manner; RTP is used for applications including dopant activation, thermal oxidation, metal reflow, chemical vapour deposition surface and bulk diffusion. In most techniques the substrate is heated from below. However, in techniques such as RIE, management of thermal energy to the substrate is necessary in order to control reaction processes, diffusion rates, or to maintain the substrate at a low temperature, often because of sensitive electronic components already fabricated on the substrate. To control the thermal energy of a substrate, a substrate holder or chuck may be used which has a thermal management system, such as process cooling, which could be a gas or liquid, to remove energy in the form of heat from the substrate, or a heating system to provide energy to heat the substrate. A good thermal contact between the substrate and chuck is arranged by introducing helium between the chuck and substrate, a technique known as helium-backside cooling. US4508161 describes a helium-backside cooling system. A seal may be used to minimise leakage of cooling gas into the process gases. A pressure detector may be used to maintain a set pressure to compensate for leakage into the process chamber as the gas seal is not perfect. This arrangement works well for maintaining the substrate at the temperature of the substrate chuck in a passive manner, but not for managing energy flow into or out of the substrate, or controlling the substrate temperature because of the high thermal mass of the chuck. The thermal management system thus set up is cumbersome and quite slow to respond, and is not suitable for fast feedback control required for active control of growth processes on a large area substrate. Other ways of delivering thermal energy to the substrate include heating from above and in this instance the temperature of the substrate can be controlled by increasing or decreasing the power of the heat source. However, control over substrate temperature is poor because the heat source is slow to respond. This inertia is associated with the large thermal capacity of the whole system that includes all of the mass components within the chamber assembly. It is known to mount a substrate on a cooled holder and vary the pressure of a gas behind the substrate to vary the thermal coupling between the substrate and holder; increasing the pressure of a gas increases its ability to conduct heat. A thermal control system for a substrate is described in US5810933. However, in such systems the thermal coupling gas must be isolated from the chamber; in many processes, for example RIE, the chamber pressure is of the order of mTorr, whereas good thermal conductivity requires several Torr of a thermally conductive gas for
effective thermal heat transfer. Furthermore, the large pressure differential between the underside of the substrate and the chamber is undesirable because this can cause stresses in the substrate.

In order to ensure that the substrate remains at the required temperature during the deposition process, accurate monitoring of the substrate temperature is required. Monitoring the substrate temperature during growth or deposition is not an easy process in PECVD or RIE systems because the plasma complicates monitoring from above, whilst embedded thermocouples or fiducial thermal markers are affected by the thermal inertia of the substrate holder, giving readings that deviate from the temperature within the substrate. Laser interferometric systems have been proposed to monitor temperatures, but these too are complicated and bulky to implement with much software related processing of two or more signals to remove the effect of the plasma from that being measured. A simple temperature measurement process that measures accurately and directly the real bulk temperatures present on materials that are used in standard semiconductor process systems is desirable.

In a PECVD system, deposition from within the plasma arises from the ionised and charged species that gain energy from the plasma and accelerated across a self bias due to its charge state. Neutral species too can take part in the process which within a plasma can create radicals. Within a plasma, which is neutral on the whole, the higher mobility electrons when compared to ions create a normally more positive potential than any object that it is in contact with. This voltage is dropped across a sheath region and ionised atoms diffusing to the edge of the sheath region feel an electrostatic force and are accelerated to the neighbouring surface. Thus all surfaces exposed to the plasma receive energetic ion bombardment which increases the density of the deposited film and helps to remove contaminants which improves the films electrical and mechanical properties. By controlling the species that take part in this process reactive etching of surfaces can also be facilitated. Parallel plate electrodes are used to capacitively couple RF and DC energy, and contain the plasma discharge between the parallel electrodes to prevent the interior of the chamber from becoming coated. Although the electrons in the plasma are very hot (around $10^3$ K) the energy coupled to the reaction surface, or growth plane is low because of the large difference in mass. Additional thermal heating may therefore
be used to increase the reaction temperature or to anneal during film growth. This heating may be provided from above the substrate, for example as described in WO 2006/120449, incorporated herein by reference in its entirety. However, in order to allow room for the top down heating elements, the upper electrode is not located directly above the lower electrode and substrate. The field is therefore distorted which can have an adverse effect on film growth.

In a PECVD system the temperature of the process gases influences the reaction efficiency, where the greater the thermal energy of the gases, the faster the reaction rate, and therefore the faster the deposition rates. In some processes it is necessary to have lower reaction rates, whereas in other processes it is desirable to have high reaction rates. Therefore, any flexibility built into the process system will improve the control and flexibility the system affords to the industry. In the cases where high reactivity of the gases is desirable, it is optimum if the gas temperature is raised at the point of delivery close to the active reaction zone of the plasma process. Ideally, the higher activation of the gases should occur within the active plasma zone of the chamber. However, the provision of a pre-heating unit increases the power requirement of the system.

PECVD systems are well suited for growing nanostructures, particularly carbon nanotubes (CNTs). There are many applications for grown carbon nanotubes in the semiconductor and sensor devices industry. However, to be useful the growth process must be CMOS and back end of line (BEOL) compatible and be able to produce CNTs over large areas, in excess of 4 inches in diameter. Conventional direct synthesis of carbon nanotubes result in higher defect levels when the synthesis temperature is matched to manufacturing constraints. The ITRS Roadmap highlights CMOS interconnects as a problem to be solved based on the current state of-the-art knowledge in the IC sector for next generation 32nm node circuits, because conventional copper or aluminium interconnects cannot support the high current densities produced at these low dimensions. By contrast, carbon nanotubes are able to support high current densities due to the covalent nature of their microstructure that prevents electro-migration of carriers. However, the synthesis temperature is critical among the various process parameters for CMOS integration compatibility. Currently, carbon nanotubes with electronic properties suitable for
interconnect applications are typically grown at temperatures of 650°C to 900°C, using backside heated bottom-up temperature sources which are not compatible with most semiconductor material systems and with CMOS/BEOL processes. At temperatures as high as these, thermal stresses and material degradation are severe and the diffusion of carefully placed dopants will take place, together with material degradation due to bond modification post-processing. Compatibility with the packaging and other back-end processing that needs to take place in the total IC process limits these temperatures to below 400°C for industrial implementation. In current low temperature synthesis of carbon nanotubes, the large area reproducibility and/or the quality of the nanotubes are not adequate, or the growth results in carbon nanofibres instead of nanotubes, with many internal material defects which affect their use as interconnects.

Carbon nanotubes may be grown in a PECVD system on a substrate which is cooled, while the necessary growth energy is supplied by the plasma. WO 03/011755 describes a low temperature CNT growth system, the contents of which are included herein by reference. An improvement to this process is to provide additional heating to the catalyst on the growth plane by heating from above the substrate while cooling from below. A top-down heating PECVD CNT growth system is described in WO 2006/120449, where the substrate is cooled while the catalyst is heated to reach its activation energy to initiate CNT growth. The energy coupled to the catalyst will not only control the quality of the material produced, but will also control the growth rates. During the growth process the energy absorption profile of the substrate changes as the ratio of chemical species on the surface of the wafer changes. It is desirable to monitor the temperature of the substrate and reduce or increase the thermal energy in the substrate accurately, in order to control the characteristics of the CNTs and manage thermal stress in the substrate. For example, CNTs for interconnects should have accurately controlled density, length, width, orientation, alignment and defect levels. The growth rate too is important to be suitable for a process window in which to grow the interconnects.
SUMMARY OF THE INVENTION

The invention is set out in the claims.

According to an aspect of the present invention, there is provided a thermal control system for a substrate, comprising a substrate holder having a surface for accepting a substrate, an energy source directed towards said surface, and a gas delivery system for introducing a gas or mixture of gases between a substrate and said surface, wherein the gas delivery system is arranged to control the thermal conductivity of the gas or mixture of gases and hence the thermal coupling between a substrate and said holder. The substrate holder acts as a heat sink. The thermal energy of a substrate on the substrate holder can be regulated by adjusting the thermal conductivity of the gas; thermal energy provided by the heat source builds up in the substrate when the gas interface between the substrate and holder is of low thermal conductivity because heat will be inhibited from flowing to the cooler sink.

Heat will be released from the substrate when the gas in the interface has a high thermal conductivity as an improved thermal path from hot substrate to holder exists.

The substrate holder may include a temperature control arrangement for controlling the temperature of the substrate holder, for example at least one conduit allowing a temperature control fluid to flow in thermal contact with the substrate holder. The temperature control arrangement ensures that the substrate holder is always held at a desired temperature. When the substrate holder is held at a low temperature, for instance by introducing cooling water at room temperature or chilled to below room temperature, the substrate holder behaves as a heat sink.

In the preferred embodiment the gas delivery system may include a controller for controlling the flow of a gas of high thermal conductivity, such as hydrogen. But, this gas does not need to be of a single elemental composition but a mixture of gases which allows for better control of the backside heating or cooling process and much faster feedback control which can be electronically coupled to a thermal measurement system and a growth process for nanomaterials where careful interfacial control between heterogeneous media is of importance. The pressure of the thermally conductive gas is a factor in determining the thermal coupling between the substrate and the holder.
The gas delivery system may comprise means for controlling the ratio of the mixture of gases to each other. At least one mass flow controller may be provided to control the flow of at least one of the gases in the mixture of gases. When the ratio of the higher thermally conductive gas to low thermal conductivity gas is high, the thermal coupling between substrate and holder is large and excess energy will flow from the substrate to the sink. When the ratio of the higher thermally conductive gas to low thermal conductivity gas is low, the substrate will be less thermally connected to the holder and thereby more isolated from the sink and the temperature of the substrate will increase due to energy input from the energy supply not matching the energy removal process at the holder. By balancing the gas ratio and energy input, the substrate temperature can be stabilised at a predetermined level. The ability to flexibly control the temperature of the growth plane by coupling feedback control to the back-side cooling thermal management system affords significant advantages.

The gas delivery system may have an output on the surface of the substrate holder, so that gas is delivered directly between the substrate and holder. This ensures that the interface between substrate and holder is well provided with thermal control gas.

The mixture of gases may be delivered to the output on the surface of the substrate holder, or a single gas may be delivered to the output on the surface of the substrate holder while another gas may be delivered to the chamber as a process gas. In general the process gas has a high conductivity, such as hydrogen, and this gas permeates beneath the substrate to provide a high degree of thermal coupling between the substrate and holder. The thermal coupling can be decreased by introducing a low thermal conductivity gas such as argon to displace the hydrogen. This works in systems where the operating pressure is in the range 1 – 500 Torr, for instance in growing CNTs, and therefore the process gas is of sufficient pressure to provide the required thermal conductivity.

The thermal control apparatus may be incorporated into a semiconductor processing apparatus and this apparatus provided in a vacuum chamber, for instance in a CVD, RIE or RTP system. The processing apparatus is preferably a PECVD system.

The substrate holder may be electrically conductive and may act as an electrode. The energy source may be a plasma and/or lamps producing IR and/or optical and/or UV light.
The thermal control gas composition and pressure can be optimised to complement the growth process gases used or be inert so as to not affect the growth process taking place in the controlled growth chamber. However, a gas seal may be provided around the substrate to minimise thermal control gas leakage into the chamber so that the thermal control gases are prevented from reaching the plasma in the PECVD system and therefore functioning in the deposition process.

The gas may be a gas of relatively high thermal conductivity such as hydrogen or helium, or may be a gas of relatively low thermal conductivity, such as argon or nitrogen.

The gas may be a process gas that is supplied to function in the PECVD process, as are many of the gases used for thermal control processing.

In another aspect there is provided a method of regulating the temperature of a substrate in a semiconductor processing system, comprising the steps of: placing a substrate on the substrate holder, heating the substrate with a heat source, introducing a gas or mixture of gases between the substrate and substrate holder and controlling the thermal conductivity of the gas or mixture of gases in order to control the thermal coupling between the substrate and substrate holder.

The method may further include the step of controlling the temperature of the substrate holder for example by cooling the substrate holder. A mixture of gases of different thermal conductivity may be provided, and the ratio of the gases adjusted in order to vary the thermal conductivity of the gas mixture. The ratio of gases may be adjusted to the extent that only a single type of gas flows. The ratio may also be subsequently adjusted so that only another single type of gas flows. This may be useful to rapidly change the thermal conductivity of the medium between the substrate and substrate holder, by providing, for example, a flow of hydrogen having a high thermal conductivity and then purging with argon which has a low thermal conductivity.

According to another aspect of the present invention there is provided a radiation measurement apparatus for measuring the temperature in the region of a layer deposited on a silicon substrate in a PECVD system, comprising a temperature regulated substrate holder having a surface for accepting a substrate, and a
radiation measuring device for measuring radiation emitted from said region, wherein the radiation measuring device includes a radiation detector which is located on the opposite side of said surface to the substrate. In this way the temperature of the layer on the surface of the substrate can be measured, because cool silicon is transparent to IR radiation and the measuring device sees the layer through the substrate. The substrate holder may include an orifice for allowing radiation emitted from the region of the layer to reach the radiation detector. A heat source may be positioned on the side of the substrate holder opposite to the radiation detector. The heat source may be a plasma and/or a lamp emitting IR and/or optical and/or UV radiation. The substrate holder may include at least one conduit allowing a temperature control fluid to flow in thermal contact with the substrate holder.

In another aspect a method of measuring radiation emitted from a region of a layer deposited on a silicon substrate in a PECVD system is provided, comprising the steps of; placing the silicon substrate in thermal contact with a substrate holder, heating the layer using a heat source positioned on the side of the layer opposite the substrate, cooling the substrate holder to maintain the temperature of the substrate at a level at which silicon is substantially transparent to a selected frequency of electromagnetic radiation, measuring the intensity of radiation emitted at the selected frequency by the region through the substrate. The measured value of intensity of radiation emitted can then be used to control the thermal energy in the substrate. The method may further comprise the step of converting the measured intensity of radiation to a temperature value, which can then be displayed or recorded.

In another aspect a PECVD system for depositing material onto a substrate is provided, comprising a first electrode arranged to support a substrate, a second electrode, an AC power supply, such as RF or pulsed DC, connected to the first or second electrode, and a heat source for providing thermal energy to a substrate when mounted on the first electrode, wherein the second electrode is disposed between the first electrode and the heat source, and wherein the second electrode is formed with a plurality of openings to allow radiation from the heat source to penetrate and reach a substrate on the first electrode. In this way the advantages of a parallel plate electrode are maintained, i.e. a regular field, while heat is applied to the substrate from the side of the substrate that requires heating, rather than the underside which often requires cooling. The size of the openings may be related to
the frequency of the power supply used. The electrode may be a mesh or a perforated sheet. The material of fabrication of the electrode may include molybdenum.

In another aspect of the present invention, an electrode is provided for use in a PECVD system which is formed with a plurality of openings, such as a mesh or perforated sheet, and wherein the size of the openings is related to the frequency of the power supply used. The electrode may be made of molybdenum.

In another aspect of the present invention there is provided a PECVD system for depositing a material onto a substrate is provided, comprising a reactor chamber, a heat source for providing thermal energy to a substrate and a gas feed system for providing process gases to the reactor chamber, wherein the gas feed system includes a gas feed tube connected to the reactor chamber, and wherein the gas feed tube is in thermal contact with the heat source to pre-heat the process gases before they enter the reactor chamber. Preheating the process gases increases the reaction efficiency and leads to higher quality materials grown thereon.

The heat source may be a lamp or lamps emitting IR and/or optical and/or UV radiation. The gas feed tube may be located in the path of the radiation when emitted from the lamp or lamps.

In another aspect, a method of operating a PECVD system for depositing material onto a substrate is provided, comprising the steps of providing thermal energy from a heat source to heat a substrate and pre-heating a process gas, such as hydrogen, with thermal energy from the heat source.

In another aspect of the present invention a PECVD system for depositing material on a silicon substrate is provided comprising a radiation measurement apparatus of the type described above arranged to measure the radiation emitted from a substrate, and a thermal control apparatus of the type described above, and a feedback controller arranged to control the thermal conductivity of the gas and the energy source of the thermal control apparatus in response to the radiation emitted from the substrate measured by the radiation measurement apparatus in order to maintain the temperature of the substrate at a preset value.
The PECVD system may have a gas inlet for introducing a carbon based gas for producing carbon nanotubes.

The PECVD system may further include an electrode having a plurality of openings, and may be formed as a mesh or a perforated sheet or other arrangement which allows IR, optical and UV radiation to directly pass through while still acting as an electrode to sustain and contain a plasma.

In another aspect, a method of operating PECVD system for depositing material on a substrate having a layer deposited thereon is provided, which includes the steps of detecting the thermal energy of the layer using the detection method described above, and regulating the temperature of the substrate using the method described above.

In another aspect, a method of preparing a substrate for use in a PECVD system for preparing carbon nanotubes is provided, comprising depositing a metal catalyst as discrete islands on the substrate and heating the catalyst in the presence of oxygen to provide a controlled oxide layer around each of the metal islands. The metal catalyst deposited could be metal clusters and thereby discrete islands prior to reaching the substrate surface or be thin metal catalyst films that will need suitable energy coupling to its surface to coax the surface to form suitable metal islands. The metal island formation from thin films could be by virtue of a reactive plasma gas treatment such as an ammonia plasma surface treatment that helps separate out thin metal layers to form a metal catalyst. All of these catalyst islands could then be oxidised to form thin conformal oxide coatings that stop it from coalescing during further processing. This oxidation shell prevents the catalyst particles agglomerating and therefore forming larger CNT's. This helps to increase CNT growth density. The Metal oxide shell is also capable of interacting preferentially with the UV part of the thermal energy source that is directed to the catalyst from above.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Embodiments of the present invention are described below, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a 2-dimensional view of the vacuum chamber of a PECVD reactor for producing carbon nanotubes in accordance with an embodiment of the invention.
Figure 2(a) is a first embodiment of a mesh electrode.

Figure 2(b) is a second embodiment of a mesh electrode.

Figure 2(c) is a schematic view of the operation of the mesh electrode with top-down heating and gas preheating from the IR source.

Figure 3 is a schematic illustration of the gas feed system.

Figure 4(a) is a simplified cross sectional view showing the gas feed to the reaction chamber where the process gases and thermal control gases are separate and the thermal control gas is fed to the underside of the substrate.

Figure 4(b) is a simplified cross sectional view showing the gas feed system of Figure 4(a), where a gas tight seal is provided between the edge of the substrate and the chuck.

Figure 5 is a graph showing how the temperature in a substrate is affected by the composition of the thermal control gas at a constant power density being delivered to the substrate.

Figure 6 is a schematic illustration of the process control system.

Figure 7 is a cross sectional view of the wafer before the PECVD growth stage.

Figure 8(a) is a graph showing how the temperature in the substrate is affected by the thickness of the thermal barrier layer at a constant power density being delivered to the substrate.

Figure 8(b) is a graph showing how the dependence of the coefficient of reflectivity on layer thickness for various types of TBL.

Figure 9(a) is a histogram showing catalyst nanoparticle size and CNT diameter.

Figure 9(b) is an SEM photograph showing CNT growth resulting from a nanoparticle catalyst pre-heated for 30 seconds.

Figure 9(c) is an SEM photograph showing CNT growth resulting from a nanoparticle catalyst pre-heated for 10 minutes.
Figure 10(a) is a cross sectional view of the temperature measuring apparatus including a substrate in place on the chuck.

Figure 10(b) is a graph showing the transmittance of a silicon wafer as a function of wavelength at different temperatures.

Figure 10(c) is a graph showing the transmission characteristics of silicon as a function of wavelength at different temperatures.

Figure 11 are graphs showing how the CNT length, lamp power and gas ratio in the system shown in Figure 1 change over time during processing.

Figure 12 is a cross sectional view of a dual chamber system in accordance with an embodiment of the invention.

Figure 13 is a SEM photograph of CNTs grown using the system shown in Figure 1.

Figures 14(a) to (c) are a series of TEM images of the grown CNTs.

Figure 15 is a plot of Raman spectroscopy data for CNTs grown using a variety of techniques.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In an embodiment of the invention, a PECVD growth system for producing nanostructures on a substrate is provided. The substrate is cooled and energy is delivered to a catalyst deposited on a growth plane on the substrate which is heated from above using an electromagnetic energy source. The electromagnetic energy source in the preferred embodiment is an optical light source that is predominantly working in the infra-red (IR) regime, but does have enhanced ultra-violet (UV) and other wavelengths that would be expected in current optical heat sources. The energy balance between the substrate and the growth plane where the nanostructures are formed, is managed by the combination of an electrically-conducting barrier-layer formed on the top surface of the substrate by controlling the temperature of the substrate from below (and above) to maintain it at a CMOS compatible temperature of, for example, 350°C. The temperature of 350°C is a general constraint imposed when processing semiconductor BEOL interconnects.
The heat from the plasma and UV/IR lamps is delivered preferentially to a catalyst layer. In an embodiment the nanostructures are carbon nanotubes (CNTs) and particularly Multi-Walled Carbon Nanotubes (MWCNTs) and Single-Walled Carbon Nanotubes (SWCNTs). The wafer rests on a liquid cooled chuck to maintain the substrate 'bulk' temperature below a reference temperature, whilst carbon nanotubes are produced of a quality associated with growth temperatures above 700°C. The process apparatus and method allows growth to be carried out more precisely at high pressures, resulting in faster growth rates and a more accurate control over the physical and electronic properties of the CNTs. The system is scalable and can grow CNTs across a large area of substrate.

In an embodiment an RF-DC plasma-enhanced chemical vapour deposition (PECVD) reactor system is used to grow carbon nanotubes. The reactor comprises a reactor chamber, a power supply system, a vacuum system, a gas feed system, a cooling system and a process control system.

The reactor chamber is shown in Figure 1. A metal vacuum chamber 101 comprises a vertical axis cylindrical body 102, with a sample stage 103 at its lower end and an IR / UV heating source 104 at its upper end. The sample stage 103 includes a substrate electrode 105 for supporting the substrate during processing, and is arranged so that a wafer installed on the electrode 105 is centrally located in the vacuum chamber 101. The electrode 105 is circular and has a flat upper surface to accept 100-300mm diameter wafers, although this is scalable to 450mm production substrates, and to even larger substrates if necessary. A clamp 106, in this example based on molybdenum is provided which rests on the rim of the electrode 105 to hold the substrate in place during processing. The underside of the electrode 105 is provided with a series of channels 107 through which temperature controlling liquid is arranged to flow; which in this embodiment is water. The electrode 105 is fabricated from a metallic compound such as stainless steel because of its ability to conduct electricity and heat effectively. The electrode 105 also has a Yttrium Aluminium Garnet (YAG) light pipe 108 which penetrates its upper and lower surfaces. The light pipe 108 is located off-centre and provides a means of monitoring radiation emitted from the underside of a substrate installed on the electrode 105. The electrode 105 is bolted to an electrical insulating structure 109 to
ensure that electrode 105 is isolated. The mounting structure 109 has flow and return conduits (not shown) to supply cooling water to the channels 107 of the chuck, and a light pipe 110 corresponding to the light pipe 108 in the chuck, for transmitting radiation.

5 A pyrometer 111 is secured to the underside of the mounting structure 109 and is capable of detecting radiation emitted from a wafer, channelled via the light pipe in the chuck and mounting structures. The pyrometer 111 has sensitive electronics and is therefore RF shielded. The pyrometer 111 is a radiation detector which is tuned to detect IR radiation of wavelength 0.9 μm. The pyrometer 111 detects the intensity of radiation emitted by an object at this wavelength, and is arranged to produce a voltage output that is proportional to temperature. The pyrometer 111 is calibrated against an aluminium freeze point thermal standard.

The mounting structure 109 is electrically bonded to the main vacuum chamber 101, and the electrode 105 has an electrical connection 112 which may be connected to an RF or DC power supply, or ground. In the present embodiment the electrode is driven by an RF source. The electrode 105 therefore acts as one plate in a capacitively coupled plasma. The cylindrical wall of the vacuum chamber 101 forms a shroud around the electrode 105 and mounting structure 109 and a gas-tight, electrically isolated connection is formed between them.

15 The cylindrical wall has optical viewports 113 for visual inspection of the chamber interior and plasma discharge. A water cooling circuit (not shown) is provided to cool the walls of the chamber during operation. A vacuum inlet (not shown) is provided connected to the vacuum pumping system.

The cylindrical wall of the vacuum chamber supports the heating source 104, which includes a lamp housing 115, an array of IR and UV lamps 116, a process gas feed 120, an upper electrode 123 and a cooling system. The lamp housing 115 is machined from a disk shaped billet of metal such as aluminium and rests on the upper rim of the cylindrical wall of the vacuum chamber 101 and is provided with sealing means to provide a gas-tight seal when locked down in an operational position. A hinged connection to the chamber wall is provided so that the heat source 104 forms a lid which may be opened to gain access to the sample stage 103. The lamp housing 115 is provided with brackets to support a cluster of eight
10kW focussed broad band heat sources 116, such as high-intensity incandescent lamps that emit strongly in the IR and UV spectrum, for example tungsten halogen bulbs. A parabolic reflective cavity is provided for each bulb 116 in the lamp housing 115 in order to concentrate the electromagnetic energy emitted by the bulbs downwards to the sample stage 103. The lamps 116 are arranged to provide an even heating across the growth plane of the substrate. UV arc sources may also be provided to increase the spectral range of the energy directed at the growth plane on the substrate. The lamp housing 115 has a water cooling circuit (not shown) to remove energy dissipating from the lamps 116 into the heat stage 104. The lamps 116 are sealed from the vacuum by a thick quartz window 119 which is a good transmitter of IR, optical and UV radiation. The quartz window 119 forms a gas tight seal with the lamp housing 115 to complete the vacuum enclosure. The quartz window 119 is penetrated by a carbon source gas feed tube 120a having a gas inlet 121 and terminating in a showerhead 122 for distributing the processes gases evenly over a wide area of the growth plane within the vacuum chamber 101.

A further process gas feed tube (not shown in Figure 1, but shown in Figure 2c as reference 120b) is formed from a length of metal tubing inside the vacuum chamber, and spiral wound around the periphery of the IR source to absorb thermal energy from the edge of the IR source, whilst not impeding the energy delivery to the substrate. The process gases can therefore be pre-heated within the vacuum chamber before entering the reactive plasma zone, to increase the reaction efficiency, leading to faster deposition rates. Alternatively the further process gas feed can be through conduits formed in the lamp housing 115 itself. The carbon source gas is not pre-heated because it can break down in the heat exchanger. Carbon source gas is fed directly to the chamber via a shower head 122 and the other process gases go via the heat exchanger.

An air filled cavity 125 is provided above the lamp housing 115 which has fans to provide further cooling of the thermal source electrical connections 104.

Bolted beneath the lamp housing 115 and extending into the vacuum chamber is an electrode clamp 124 which supports a mesh electrode 123. The mesh electrode 123 is shown in Figure 2(a). It is made of molybdenum, which is a thermally stable and electrically conductive material. Other suitable materials include, but not limited to,
silicon carbide, tantalum, stainless steel, inconel, graphite and pyrolytic graphite. Openings of approximately 5mm across are formed in the electrode. Figure 2(b) shows an alternative embodiment where a flat disk is provided with cut-out holes. The size of the openings or holes is determined by the frequency of the RF supply; in the present embodiment the openings are optimised for an RF supply of 13.56 MHz. Despite being a mesh the electrode behaves as a plate. The spaces in the mesh allow the transmission of 82% of the thermal radiation from lamps through to the substrate surface. The plane of the mesh electrode 123 is parallel to the flat surface of the electrode 105, and is arranged to be 1 cm, but can vary from 0.5 cm to 10 cm from the growth plane of the substrate across the entire area of the substrate when the heat stage 104 is locked down. The mesh electrode 123 is electrically connected (or isolated from) to the main vacuum chamber structure 101, and may be either connected to earth or to an RF or DC power supply and driven. The mesh electrode 123 is electrically connected to the chamber if it is acting as a ground electrode. If it is being driven with RF/DC energy it will be isolated from the chamber. In the present embodiment the mesh electrode 123 is grounded and the electrode 105 is driven. During operation the mesh electrode contains the plasma in a well defined zone above the substrate in the same way a plate electrode would; the electric field is therefore highly uniform across the substrate and CNTs grown thereon are well aligned. Figure 2(c) shows a schematic view of the electric field between the electrodes and also the electromagnetic field from the heating lamps 116. The confined plasma also prevents build-up of carbon on the walls of the chamber 101 and quartz window 119, as the reaction site is confined above the substrate. A build-up of carbon on the quartz window is undesirable because carbon strongly absorbs IR radiation, which reduces the energy available at the growth plane and causes excessive heating of the quartz window 119.

Power is provided to the wafer electrode 105 for sustaining a plasma from a 600W RF power supply unit at an frequency of 13.56 MHz. Alternative power supplies and supply settings may be used, particularly in a system for processing 300mm wafers, where considerably greater power is required. The power is supplied to the heating lamps under the control of a thyristor and a computer.
The vacuum system comprises a rotary pump for achieving pressures between 1 and $10^2$ Torr and a turbo pump for achieving downstream pressures in the chamber of between $10^{-2}$ and $10^{-7}$ Torr.

The gas feed system is shown schematically in Figure 3. Gases are provided in conventional high pressure bottles 301a to d. Process gases include a carbon source, such as acetylene or methane 301a, and the reactant gas such as hydrogen 301b. Thermal control gases are hydrogen 301c which has a high thermal conductivity (0.18 W/mK) and argon 301d which has a low thermal conductivity (0.017 W/mK). The output from each bottle is pressure regulated and connected to filters 302a-d. Filters 302a-d are connected to mass flow controllers 303a-d, which can control the flow of gas under external electronic control. In the present embodiment the thermal control gases are combined at a manifold 304 and piped to the gas inlet 401, as shown schematically in Figure 4(a).

Under vacuum, thermal contact between the substrate and electrode 105 is limited because surface imperfections on both the substrate and chuck create a stand-off gap. When thermal control gases are introduced into the chamber 101 via gas inlet 401, they permeate into the gap between the substrate and electrode 105. If the gases have a high thermal conductivity the thermal contact between the substrate and electrode 105 will be high as thermal energy is efficiently transmitted through the intermediate gas layer. When the thermal conductivity of the intermediate gas is poor then thermal contact between the substrate and electrode 105 is also poor and thermal energy flow will be reduced between the two components. For a hot substrate and a cooled electrode 105, the flow of heat from the substrate to the electrode 105 can therefore be controlled by adjusting the composition of the gas in the gap between the substrate and electrode 105. Therefore by controlling the ratio of thermal control gases the thermal coupling between the substrate and the chuck can be controlled and hence the thermal energy in the substrate regulated. The response time is fast in comparison to other methods of regulating the substrate temperature, such as heating or cooling the electrode 105 or adjusting the power to the IR lamps 116; as the ratio of thermal control gases is changed at the mass flow controllers 303c-d, the composition of the gas in the chamber and hence between the substrate and chuck changes effectively instantaneously because of the low
pressure conditions in the chamber 101, and therefore this technique gives precise
and rapid control over the thermal energy levels in the substrate.

Other gases with high thermal conductivity such as helium, and low thermal
conductivity such as argon and nitrogen can be used.

The mass flow controllers 303c and 303d determine the ratio of one thermal gas to
another under control of the computer and also a proportional integral differential
(PID) controller. The thermal control gas feeds to the chamber 101 are separate
from the process gas feeds; the thermal control gas mixture is fed to an inlet 401 in
the sample stage 103 and piped through the mounting structure 109 to an inlet in the
electrode 105. The thermal control gases can then be fed directly to the underside
of the substrate. The process gases are connected to feeds 120a and 120b as before.
 In a further embodiment shown in Figure 4(b) a gas-tight seal 402 is
provided around the substrate to minimise mixing of the thermal control and process
gases in the chamber 101. In this way the pressures and compositions of both gas
feed systems can be isolated to allow greater control over the growth conditions
within the reactor system. By controlling the ratio of the two thermal control gases
beneath the substrate, rather than the pressure of a single gas, the pressure on
either side of the substrate in this sealed arrangement can be balanced.

Pressure sensors (not shown) are provided to measure the pressure within the
chamber 101 and between the electrode 105 and the substrate, and are in
communication with the mass flow controllers 303a-d and arranged to maintain the
gas pressure in the chamber and between the electrode 105 and substrate at a
predetermined level.

Figure 5 shows the effect that process gas type and pressure has on thermal
coupling efficiency between the substrate and chuck. It can be seen that the
pressure of H₂ in the chamber has a dramatic effect on the thermal coupling between
the substrate and chuck, while argon pressure is less effective. Thermal coupling
can be controlled by regulating the hydrogen pressure in the chamber alone.
However, it is often required to maintain a constant pressure in the chamber and
therefore mixing H₂ and Ar and adjusting their ratios is an effective method of
controlling thermal coupling between substrate and chuck.
The PECVD process is controlled by a process control system, shown schematically in Figure 6. A central computer 601 is connected to and is able to control the gas supply mass flow controllers 303a-d, the plasma power supply, the heating lamp power supply and the vacuum pumps. The computer 601 receives data from the pyrometer 111 for monitoring the substrate temperature, a chamber pressure sensor 602 and a power sensor 603 to monitor the power consumed by the heating lamps 116. A pressure sensor 606 is provided to measure the pressure of the thermal control gases. The computer 601 has stored a number of reaction schedules or recipes which carry out predetermined instructions depending on products required. A user interface is also provided where process parameters can be entered and varied manually. Variables in the process include type, delivery rate and pressure of process and thermal control gases, energy delivery levels and substrate temperature, all of which may be time varying. The computer operating system is compatible with a known SEMI interface and therefore the system may be integrated with other semiconductor processing tools and high volume manufacturing cluster platforms, particularly for Back End Of Line (BEOL) interconnect production.

The computer 601 is arranged to control the power to the lamps 116 by thyristor 604. The computer controls the mass flow controllers 303a-d to determine the carbon content in the reaction and thermal control gas ratio.

The substrate temperature is controlled by a proportional integral derivative (PID) controller 605. The process variable (PV) to the PID 605 is temperature as determined by the pyrometer 111, and the manipulated variables (MV) are the power supplied to the lamps 116, controlled by a thyristor 604 and the thermal gas ratio, controlled by mass flow controllers 303c, d. The set point (SP) of the PID 605 is 350°C and the PID 605 controls the power to lamps 116 and the thermal gas ratios to maintain the temperature of the substrate at the set point.

The set point, i.e. the maximum temperature of the substrate as measured by the pyrometer, will vary from substrate to substrate. The temperature reading from the pyrometer is dependent on the physical properties of the substrate and substrate material, thickness, doping levels and doping profile will all affect the apparent temperature measured by the pyrometer. Also some substrates are more sensitive
to others to temperature. Therefore a calibration run is performed to confirm the set point for a particular substrate.

The substrate used may be a pure silicon wafer, or any other wafer, or the wafer may have been pre-treated and doped. The substrate may also have been extensively treated in other fabrication processes to produce a complex array of junctions forming components such as transistors, diodes or other CMOS integrated circuits.

Prior to growth of the carbon nanotubes, the substrate is prepared as shown in Figure 7. Substrate 701 is provided with a thermal barrier layer 702 (TBL) and a catalyst layer 703. The thermal barrier 702 is sputtered, but can be created in a number of other manners such as thermal evaporation or electrochemical deposition, onto the substrate 701 and is an electronically conductive, thermally insulating, optically reflective layer grown on the substrate 701 to further protect the substrate 701 during heating of the catalyst 703. A detailed discussion of a suitable thermal barrier layer 702 is given in WO 2006/ 120449 which is incorporated herein by reference. The thermal barrier layer 702 also restricts bulk diffusion between the catalyst 703 and substrate 701. A suitable material for the barrier layer 702 is Ti, which may be coated with a further layer of TiN, or TiO₂. Alternatively Ta, TaN or TaO₂ may be used. Figure 8(a) shows the effect of TBL thickness on substrate temperature, where the change in temperature of the substrate over time for various thicknesses of Ti thermal barrier can be seen. In general, as the barrier layer gets thicker, most of the radiation is reflected, as the optical reflectivity of the barrier increases with thickness.

Figure 8(b) shows the reflection coefficient calculated for 825nm wavelength p-polarised light incident at 45° for three different material. TiO₂ can be seen to provide the greatest reflectivity for a given thickness.

A catalyst is deposited on the thermal barrier layer to provide a nucleation site for carbon nanotube growth. The catalyst layer 703 is therefore the growth plane, and the thermal energy provided by the system, i.e. from the IR/UV lamps 116, the plasma and the chemical deposition reaction itself is directed towards this plane. The thermal barrier layer 702, cooled electrode 105 and gas ratio control regulate the effect of this thermal energy on the substrate. The catalyst 703 may be a metal
or a mixture of metals, preferably a transition metal such as Ni, Fe or Co for the
growth of CNTs. For the growth of silicon nanowires, Ga or Au may be used. The
catalyst 703 may be formed on the TBL 702 as a continuous layer. Preferably
however, the catalyst 703 is provided as an evenly distributed layer of discrete
metallic islands. This is because a CNT can preferentially nucleate and grow from a
single island. The density and diameter of the grown CNTs is related to the size and
density of the catalyst islands; a high CNT density of $10^{12}$ per square cm is desirable.
The catalyst deposition technique should be cost effective and introduce minimal
thermal stress to the structure. Techniques such as sputtering and e-beam vapour
deposition require high temperature post annealing to form the required islands.
Electrochemical deposition is a wet process that requires a wet electro chemical
deposition equipment, and the process chemistry is complex. Electron beam direct
write lithography could be used but is slow. In an embodiment, a metal powder is
used to coat the thermal barrier layer 702. In a preferred embodiment nanoparticles
of the catalyst are condensed from the vapour state onto the thermal barrier layer
702. It is possible to control the size distribution of the particles to within 10%.
Deposited particles carry a charge and it is therefore also possible to control the
landing energy and allow a "soft or hard landing" of the particles on the TBL 702, or if
they are accelerated at the base of a trench (not shown) in the substrate for
example. The vapour condensation process may be carried out at room temperature
and therefore does not have an adverse effect on the substrate itself.

The regular array of metallic catalyst 703 on the thermal barrier layer 702 acts as a
plasmonic surface, which allows for preferential coupling of the electromagnetic
radiation from the heating lamps 116. The absorption of thermal energy from the
lamps 116 is enhanced by the presence of nanoparticles because they exhibit strong
absorption bands that are not present in the bulk metal. Typically this is in the UV/
optical part of the spectrum; the heating system can be tuned to exploit this effect or
further heating elements that emit in different parts of the electromagnetic spectrum
can be used, coupling energy efficiently by emitting at the absorption energy of the
nanoparticle catalyst.

Thermal barrier layer sputtering, vapour condensation of the catalyst and PECVD of
carbon nanotubes may be undertaken in separate reaction chambers. In this
instance the substrate is transferred in air from one chamber to another. In an
embodiment, the sputtering and vapour deposition stages are undertaken in the same reaction chamber and the PECVD in a separate reactor, the substrate transferred through air between the Thermal Barrier Layer/ catalyst deposition stages and the CNT growth stage.

In operation, the substrate 701 is placed in a vacuum chamber which is pumped to $10^{-5}$ Torr. The vacuum chamber contains sputtering and vapour deposition apparatus. The substrate is first pre-cleaned and de-gassed by a UV and IR source to remove water vapour from the substrate surface. The surface is then RF sputter etched to promote adhesion of the TBL. The TBL is then formed by reactive sputtering until the required thickness is achieved.

For depositing the barrier layer, example sputtering conditions are: an argon sputter gas flow of 16 sccm argon and nitrogen flow of 31 sccm. A target material of Ti and target voltage typically 340 volts at 4 mTorr. The barrier deposition time is typically 75 seconds. Example PVD nano particle catalyst deposition conditions are: sputtering pressure of 50 mTorr and the metal vapour transits a helium cooled agglomeration zone which condenses the metal vapour into metallic clusters, where agglomeration zone gas flow is 10 sccm Helium. The target voltage is 320V DC which produces a deposition rate of 0.5 -3nm per min.

The chamber is then returned to atmospheric pressure and the treated substrate is transferred to the PECVD reactor chamber shown in Figure 1.

The treated substrate 700 is placed on the electrode 105 and clamped in place with the molybdenum clamp 106. The heating stage 104 is then lowered into place on the chamber wall and locked down. The chamber 101 is evacuated to a pressure of $10^{-5}$ Torr. The cooling water is turned on to maintain the temperature of the electrode 105, vacuum chamber walls and heating stage 104 at 25°C. Bulk H$_2$ process gas is introduced at a rate of 250 sccm. H$_2$ and Ar thermal control gas flow is introduced at the feed point between the electrode 105 and substrate at 50 sccm and at working pressure of 5 Torr set. The ratio of H$_2$ to Ar is initially maintained at around 1:9, so that Ar dominates and therefore the gas mixture has a low conductivity; the thermal coupling between the substrate and electrode 105 is therefore low at this initial stage and the substrate 700 is thermally isolated. This
procedure is part of the startup process to enable the back-side cooling and the catalyst and substrate temperatures to be maintained to conform to the requirements for CMOS and BEOL processing. Power is then provided to the heating lamps 116 to deliver energy to the catalyst 703. The catalyst 703 absorbs the electromagnetic radiation, while the thermal barrier layer 702 reflects a proportion back into the catalyst 703 away from the substrate 701. After 5 seconds of lamp heating then an arc suppressed DC plasma is struck between the electrode 105 and the mesh electrode 123 at a constant 550 V. Energy from the plasma couples to the catalyst 703, increasing the energy in the catalyst layer. The energy in the catalyst layer needs to be high enough to reach the activation energy for CNT growth all across the substrate 700. After a 5 second stabilisation delay, acetylene is delivered at a rate of 22 sccm to the chamber by the mass flow controller 303a. This rate is selected as a proportion of the bulk process gas and could range from 0.5 sccm to 100 sccm depending on the characteristics of the CNTs that it is intended to produce and the size of the substrate. Process gas ratios are known in the art.

Initially the emissivity of the growth plane is low, because it comprises Ni, Co or Fe catalyst on a highly reflective layer 702. The energy coupling between the catalyst and heat sources is therefore low. The Ni catalyst 703 scatters IR energy while most is reflected by the TBL 702. The initial heating is insufficient for nanotube growth because the activation energy for growth is not yet reached, but the heating is enough to initiate the aggregation of some Ni catalyst particles. The thermal energy of the catalyst particles is therefore increased rapidly to the CNT growth activation point so that CNTs start to grow around the catalyst islands and inhibit agglomeration of the catalyst. Agglomeration is undesirable because it increases the size of the catalyst particles, and decreases their density, which reduces the density of the grown nanotubes and increases their diameter. Figure 9(a) shows the histogram of as-deposited catalyst nanoparticles and nanotube particle diameter distribution. The Ni particles have a mean diameter of 7.4nm with a standard deviation of 1.4nm (from 80 nanoparticles). The nanotubes have a mean diameter of 17.4nm and a standard deviation of 6.4nm (from 70 nanotubes), where during the initial period of broadband IR irradiation, the Ni nanoparticles on the surface heat up and agglomerate. The TEM analysis indicates that the nanotube catalyst particles grow in size by about 130% from its original mean size of 7.4nm to 17nm. The
agglomeration is thermally driven, but limited by the reaction time in this configuration. Typically, a 5nm thick catalyst thin film can form particles with sizes up to hundreds of nanometres with conventional furnace heating. Increasing the time between the powering up of the lamps to the introduction of the acetylene (to initiate the growth) from 30s to 10mins shows a dramatic increase (~1305%) in the mean nanotube diameter to 104nm (standard deviation of 32nm) as can be seen in Figure 9(b) and 9(c). Figure 9(b) shows CNTs grown from a catalyst that has been pre-heated for 30 seconds, whereas Figure 9(c) shows CNTs grown from a catalyst that has been pre-heated for 10 minutes. The lamps 116 are therefore used on full power to pre-heat the substrate for a period of 30 seconds.

As the plasma starts to deposit carbon onto the Ni catalyst, the carbon increases the absorption of IR energy and the emissivity of the growth plane goes down. The heat acquired is lost both through the surrounding process gasses and thermal conductance through the TBL 702 into the substrate 701. When the temperature reaches a sufficient level the nanotubes start to nucleate and grow over the whole area of the substrate 701 in regions where the catalyst 703 is provided. For the gas pressures used, growth rates of 1-5 μm/ min are possible. As the nanotubes increase in length they absorb further IR energy leading to the annealing of defects.

As the material growing on the catalyst absorbs more IR radiation the temperature of the substrate 701 measured by the pyrometer 111 increases.

Figure 10(b) shows how the temperature of the silicon substrate close to the barrier layer is measured. The transmittivity of silicon to IR radiation is high at low temperatures, as can be seen in Figure 10(b). Therefore initially, when the temperature of the substrate 701 is low the IR transmission of the substrate 701 is high and the pyrometer 111 measures the temperature of the TBL 702 by detecting radiation emitted from the TBL 702. As the temperature of the TBL 702 increases the temperature of the substrate also rises. An increase in the thermal energy of the substrate will decrease its IR transmittivity and therefore the relative point of temperature reading will descend through the substrate 700 from the TBL 702 contacting surface towards the surface in contact with the electrode 105. When the substrate 700 is heated to around 400°C the pyrometer effectively measures the bulk temperature of the substrate as it is then fully opaque. However, the PID does not
allow the temperature of the substrate to go above the SP of 350 °C. The PID maintains the temperature of the substrate at an optimal 350°C by controlling the H₂:Ar ratio and the power supplied to the heating lamps 116. Therefore the substrate always remains partially transparent and the temperature as measured by the pyrometer 111 is that of the substrate at around 1/3 depth from the TBL 702 interface. The transmission of silicon at around these temperatures is shown in Figure 10(c).

As the temperature of the substrate increases, the ratio of H₂:Ar is increased to 9:1 so that the gas mixture has a high thermal conductivity and thermal energy in the substrate 700 will flow to the cooled electrode 105. At the same time power to the lamps 116 can be reduced. The thermal control gas ratio is then adjusted to selectively slow the CNT growth to a sustainable rate, so that the energy coupling from the lamps 116 to the catalyst 703 is optimal while substrate temperature is maintained at 350°C. This high level of process control reduces the thermal stresses in the substrate and compensates for the thermal mass of the heating system, which is not responsive enough to prevent overheating of the substrate.

At the end of the growth process after around 250s the power to the lamps 116 is turned off. It is desirable to halt the growth process abruptly, as excedent heat in the nanotubes can cause the growth process to continue and introduce defects. Therefore the thermal gas control ratio is adjusted to allow pure hydrogen to flow between the substrate 700 and electrode 105 in order to maximise thermal coupling and thus rapidly remove thermal energy from the substrate for fast process termination.

The chamber 101 can then be returned to atmospheric pressure, the heating source 104 lifted clear of the wafer, the clamp 106 removed and the processed substrate 700 removed from the system.

Figure 11 summarises in a graphical form the variation in lamp power and gas ratio throughout the process, and how this relates to the CNT length.

When the substrate is first loaded it has a very reflective surface like a mirror. The thermal sources are not efficient at heating the surface as much energy is reflected back to the chamber. At this point in time the substrate has a low emissivity surface
(reflective) and the heat sources need to provide a lot of energy to heat the wafer up. The UV part of the thermal source is more effective at heating the mirror surface. Once CNT growth starts the surface transitions to a high emissivity surface (almost a black body). This surface easily absorbs IR energy so the lamp control system needs to rapidly reduce power to prevent the substrate from overheating. It is difficult for the lamps and filaments to dissipate energy quickly to prevent overheating of the substrate because of their thermal mass. Therefore providing a low thermal conductivity gas at low emissivity helps heat the catalyst, and then transitioning to a high thermal conductivity gas mixture once CNTs are well established helps to maintain the substrate at a set temperature. This is an active (not passive like backside cooling) method of controlling energy build up in the substrate under a wide range of emissivity conditions found when growing CNTs, where the energy is provided from above the catalyst.

Referring to Figure 11, initially the lamp power is increased rapidly and the gas is thermally insulating to increase the energy in the catalyst. The carbon gas flow is turned on and for a period there is no growth, while the activation energy of the catalyst is attained. When CNTs start to grow after around 30s, the gas ratio is adjusted to drain thermal energy that has started to build up in the substrate, and the lamp power is reduced.

An equilibrium is then maintained between input lamp power and growth rate as the growing CNTs absorb more thermal radiation as their length increases. When the required CNT length is reached, the process is terminated by switching off the lamps and adjusting the gas ratio to thermally conductive to remove energy from the substrate and hence from the growth plane.

In another embodiment a dual chamber system is provided so that the growth of the thermal barrier layer 702, catalyst 63 and carbon nanotubes takes place in a controlled environment. A suitable system is shown in Figure 12. A preparation module 1201 is provided for sputter coating the TBL 702 and vapour condensation of the catalyst 703, and a second connected module 1202 for the PECVD of CNTs. The substrate remains under vacuum or in a controlled atmosphere between all of the deposition stages.
The TBL and catalyst are deposited in the preparation module 1201 as described above. However, a controlled amount of oxygen is introduced to the system and a short heat pulse provided to create an oxide layer of known thickness around each of the deposited catalyst islands. The oxide layer around the catalyst prevents agglomeration during the initial heating of the catalyst. Agglomeration can reduce the density of the grown CNTs. During processing the carbon gas can diffuse through the oxide layer to the metallic catalyst core and nucleate CNT growth. Furthermore, coupling of the electromagnetic radiation from the lamps 116 with the plasmonic surface of the catalyst can be influenced by the thickness of the oxide layers.

In another embodiment, only a single low thermal conductivity gas, such as argon, is provided at the inlet 401 beneath the substrate. The high thermal conductivity gas is provided as a process gas from inlet 102b at a constant pressure. The variation in gas ratio beneath the substrate is provided by varying the pressure of the argon supply. When good thermal coupling between the substrate and holder is required, the argon pressure is low or zero, so that the space between the substrate and electrode is occupied by the high thermal conductivity process gases, including hydrogen. When it is desired to reduce the thermal conductivity between the substrate and electrode, the argon pressure is increased and argon is introduced to displace the hydrogen process gas.

The resulting CNTs are shown in Figure 13, which is a scanning electron micrograph of low temperature, growth of high quality carbon nanotubes which can be scaled to 4 inch and larger substrates. The growth is not limited by the catalyst diameter and their length increases with the growth time. The growth rate can be controlled from around 1nm/min to 1500nm/min based on the growth condition and energy coupled to the surface of the catalyst. TEM analysis confirms that the deposited catalyst nanoparticles are crystalline. The nanotubes can be vertically aligned and follow a tip or base growth method (catalyst dependent), based on the deposition conditions and the catalyst used.

Figure 14 shows Raman spectroscopy data which indicates that the nanotubes grown in the above process have a similar quality to those grown at temperatures higher than 700°C through the presence of both first order and distinct second-order
Raman peaks. The material is of high quality with clear Raman radial breathing modes present in the spectrum indicative of single walled carbon nanotube growth in this sample.

It is to be understood that various modifications to the preferred embodiment and the generic principles and features described herein will be readily apparent to those skilled in the art. Thus, the present invention is not intended to be limited to the embodiment shown and such modifications and variations also fall within the spirit and scope of the appended claims.
CLAIMS

1. A thermal control system for a substrate, comprising:
a substrate holder having a surface for accepting a substrate, an energy source
directed towards said surface, and a gas delivery system for introducing a mixture of
gases between a substrate and said surface, wherein the gas delivery system
includes gas ratio control means to control the ratio of said mixture of gases to each
other and hence the thermal coupling between a substrate and said holder.

2. A thermal control system for a substrate in accordance with claim 1, wherein
the substrate holder includes a temperature control arrangement for controlling the
temperature of the substrate holder.

3. A thermal control system for a substrate in accordance with claim 2, wherein
the temperature control arrangement includes at least one conduit allowing a
temperature control fluid to flow in thermal contact with the substrate holder.

4. A thermal control system for a substrate in accordance with any preceding
claim, wherein said gas ratio control means includes at least one mass flow
controller to control the flow of at least one of the gases in the mixture of gases.

5. A thermal control system for a substrate in accordance with any preceding
claim, wherein the gas delivery system includes an output on said surface of the
substrate holder, so that in use gas is delivered directly between a substrate and the
holder.

6. A thermal control system for a substrate in accordance with any preceding
claim, wherein the thermal control system is incorporated in a substrate processing
apparatus.

7. A thermal control system for a substrate in accordance claim 6, wherein the
substrate processing apparatus is provided in a vacuum chamber.

8. A thermal control system for a substrate in accordance with claim 7 wherein
the gas delivery system includes a gas output into the vacuum chamber.

9. A thermal control system for a substrate in accordance with any of claims 6 to
8, wherein the substrate processing apparatus is a PECVD system.
10. A thermal control system for a substrate in accordance with any preceding claim, wherein the substrate holder is electrically conductive.

11. A thermal control system for a substrate in accordance with claim 10, wherein the substrate holder is an electrode.

12. A thermal control system for a substrate in accordance with any preceding claim, additionally comprising a seal for a substrate to reduce, in use, the amount of said gas or mixture of gases from reaching the face of the substrate which is not in contact with the substrate holder.

13. A thermal control system for a substrate in accordance with any preceding claim, wherein the energy source includes a plasma.

14. A thermal control system for a substrate in accordance with any preceding claim, wherein the energy source includes a heating lamp producing electromagnetic radiation in the form of IR radiation.

15. A thermal control system for a substrate in accordance with any preceding claim, wherein the energy source includes a source of UV and/ or optical electromagnetic radiation.

16. A method of regulating the temperature of a substrate in a semiconductor processing system, comprising the steps of: placing a substrate on a substrate holder, heating the substrate with a heat source, introducing a mixture of gases between the substrate and substrate holder and controlling the ratio of the gases to each other in order to control the thermal coupling between the substrate and substrate holder.

17. A method of regulating the temperature of a substrate in a semiconductor processing system in accordance with claim 16, comprising the step of controlling the temperature of the substrate holder.

18. A method of regulating the temperature of a substrate in a semiconductor processing system in accordance with claim 17, wherein the substrate holder is cooled.
19. A method of regulating the temperature of a substrate in accordance with any of claims 16 to 18, comprising the step of introducing the mixture of gases directly between the substrate and the substrate holder.

20. A method of regulating the temperature of a substrate in accordance with any of claims 16 to 18, comprising the step of introducing one of the gases of the mixture of gases directly between the substrate and the substrate holder and another of the gases of the mixture of gases outside the periphery of the substrate and substrate holder.

21. A radiation measurement apparatus for measuring the radiation emitted from a region of a layer deposited on a silicon substrate in a PECVD system, comprising a temperature regulated substrate holder having a surface for accepting a substrate, and a radiation measuring device for measuring radiation emitted from said region, wherein the radiation measuring device includes a radiation detector which is located on the opposite side of said surface to the substrate.

22. A radiation measurement apparatus in accordance with claim 21, wherein the substrate holder includes an orifice suitable for allowing radiation emitted from said region to reach the radiation detector.

23. A radiation measurement apparatus in accordance with claims 21 or 22, including a heat source positioned on the side of the substrate holder opposite to the radiation detector.

24. A radiation measurement apparatus in accordance with claim 23 wherein the heat source is a plasma.

25. A radiation measurement apparatus in accordance with claim 23 or 24, wherein the heat source is a lamp emitting IR and/or optical and/or UV radiation.

26. A radiation measurement apparatus in accordance with any of claims 21 to 25, wherein the substrate holder includes at least one conduit allowing a temperature control fluid to flow in thermal contact with the substrate holder.

27. A radiation measurement apparatus in accordance with any of claims 21 to 26, further comprising means for converting the measured radiation to a temperature value.
28. A method of measuring radiation emitted from the region of a layer deposited on a silicon substrate in a PECVD system, comprising the steps of; placing the silicon substrate in thermal contact with a substrate holder, heating the layer using a heat source positioned on the side of the layer opposite to the substrate, cooling the substrate holder to maintain the temperature of the substrate at a level at which silicon is substantially transparent to a selected frequency of electromagnetic radiation, and measuring the intensity of radiation emitted at the selected frequency by the region through the substrate.

29. A method of measuring radiation in accordance with claim 28, comprising converting the measured intensity of radiation to a temperature value.

30. A method of measuring radiation in accordance with claim 28 or 29, wherein the selected frequency of electromagnetic radiation corresponds to IR radiation.

31. A PECVD system for depositing material onto a substrate, comprising a first electrode arranged to support a substrate, a second electrode, an AC power supply connected to the first or second electrode, and a heat source for providing thermal energy to a substrate when mounted on the first electrode, wherein the second electrode is disposed between the first electrode and the heat source, and wherein the second electrode includes a plurality of openings to allow radiation from the heat source to reach the first electrode.

32. A PECVD system for depositing material onto a substrate in accordance with claim 31, wherein the AC power supply is a Radio Frequency power supply.

33. A PECVD system for depositing material onto a substrate in accordance with claim 31 or 32, wherein the size of the openings is related to the frequency of the power supply.

34. A PECVD system for depositing material onto a substrate in accordance with any of claims 31 to 33, wherein the second electrode is a mesh.

35. A PECVD system for depositing material onto a substrate in accordance with any of claims 31 to 34, wherein the second electrode is a perforated sheet.

36. A PECVD system for depositing material onto a substrate in accordance with any of claims 31 to 35, wherein the second electrode is comprised of molybdenum.
37. A PECVD system for depositing a material onto a substrate, comprising a reactor chamber, a heat source for providing thermal energy to a substrate and a gas feed system for providing process gases to the reactor chamber, wherein the gas feed system includes a gas feed tube in communication with the reactor chamber, and wherein the gas feed tube is in thermal contact with the heat source to pre-heat the process gases before they enter the reactor chamber.

38. A PECVD system for depositing a material onto a substrate in accordance with claim 37, wherein the heat source is at least one lamp emitting IR and/or optical and/or UV radiation.

39. A PECVD system for depositing a material onto a substrate in accordance with claim 37 or 38, wherein the gas feed tube is located in the path of the radiation emitted from the lamp or lamps.

40. A PECVD system as claimed in any one of claims 31 to 39 including a gas inlet for introducing a carbon based gas for producing carbon nanotubes.

41. A PECVD system as claimed in any one of claims 31 to 40 including an electrode having a plurality of openings to allow the passage of radiation from the heat source.

42. A method of operating a PECVD system for depositing material onto a substrate, comprising the steps of: providing thermal energy from a heat source to heat a substrate, and pre-heating a process gas with thermal energy from the heat source.

43. A PECVD system for depositing material on a silicon substrate comprising a thermal control system as claimed in any one of claims 1 to 15, a radiation measurement apparatus as claimed in any one of claims 21 to 27 for measuring the radiation emitted from a substrate, and a feedback controller arranged to control the thermal control apparatus in response to the radiation emitted from the substrate in order to maintain the temperature of the substrate at a preset value.

44. A method of operating a PCVD system for depositing material on a substrate having a layer deposited thereon, including measuring radiation emitted by the layer
as claimed in any of claims 28 to 30 and regulating the temperature of the substrate as claimed in any of claims 16 to 20 in dependence on the measured radiation.

45. A method of preparing a substrate for use in a PECVD system for preparing carbon nanotubes, comprising controlling the temperature depositing a metal catalyst as discrete islands on the substrate and heating the catalyst in the presence of oxygen to provide a controlled oxide layer around each of the metal islands.

46. An electrode suitable for use as the second electrode in the PECVD system of any of claims 31 to 41.

47. A nanomaterials growth system as herein described and illustrated in accompanying Figures 1 to 15.
Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

<table>
<thead>
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<th>Category</th>
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<tr>
<td>X,Y</td>
<td>X: 1-9 and 13-20; Y: 43</td>
<td>EP0397315 A2 (APPLIED MATERIALS) Abstract, figure 2, column 1 lines 7-19, column 3 line 40 - column 4 line 31, column 8 lines 19-38</td>
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<td>X,Y</td>
<td>X: 21-25 and 27; Y: 26 and 43</td>
<td>US2001/014111 A1 (SHIMIZU) Abstract, figure 5, paragraphs 2, 10, 11, 80-84 and 89</td>
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(SURREY NANOSYSTEMS) Abstract, figures 5 and 8, page 17 lines 13-18

A |   | US2005/223994 A1
(BLOMILEY) Abstract, figure 12, paragraphs 78-80

A |   | JP11153489 A
(KOKUSA1) WPI abstract, figure 6

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Claims searched: 45  
Examiner: Dr Paul Baxter  
Date of search: 30 June 2010

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