Low temperature process for depositing oxide layers by photochemical vapor deposition

This invention is concerned with a process for forming oxide layers on substrate surfaces and is useful, for example in the manufacture of semiconductor devices for forming a dielectric oxide layer on the surface of a selected semiconductor material and in the manufacture of optical elements.

In the manufacture of semiconductor devices, it is frequently necessary to form a dielectric layer either as a passivation layer to permanently protect the surface of the substrate or as a mask during such procedures as etching, solid state diffusion, or ion-implantation. One method by which an oxide layer, such as silicon dioxide (SiO_2), may be formed is a plasma-enhanced chemical vapor deposition process as described by James A. Amick, G. L. Schnable, and J. L. Vossen, in the publication entitled, "Deposition Techniques for Dielectric Films on Semiconductor Devices", in the Journal of Vacuum Science Technology, Vol. 14, No. 5, Sept.—Oct. 1977, pp. 1053—1063. In such a plasma-enhanced process, the vapor phase reactants, such as silane (SiH_4) and nitrous oxide (N_2O), are subjected to a radio frequency discharge, which creates an ionized plasma of the reactant gases. These ionized reactants then interact to form the desired reaction product. However, as a result of the exposure of the reactant gases to the radio frequency discharge, numerous extraneous ionized and neutral particles, as well as high energy radiation with wavelengths as low as 500 angstroms (Å) and even extending into the x-ray region, are produced and bombard the surface of the substrate on which the oxide is being formed. If the substrate comprises a sensitive device type, such as a charge coupled device or a device formed of certain compound semiconductors (e.g., InSb, HgCdTe, or GaAs), the above-described charged particles and unwanted radiation frequently impart damage to these sensitive devices. For example, the deposited oxide layer may incorporate charges or dangling bonds, which create high surface state densities (N_{ss}) at the semiconductor device/oxide layer interface and which will trap charges when a voltage is applied to the device, thereby preventing optimum device performance. In addition, a plasma enhanced deposition process has the disadvantage that plasma-induced heating of the substrate occurs as a result of selective absorption of the radio frequency energy by the substrate, and this heating causes uncertainty in the temperature of the substrate, which prevents optimization of the characteristics of the deposited oxide layer.

Other methods by which oxide layers may be formed use a non-reactive or a reactive sputtering technique. By a non-reactive sputtering technique, as described, for example, by Amick et al as referenced above, a disk of the selected oxide material, such as SiO_2, is bombarded with argon ions, which cause the SiO_2 to vaporize, and the vaporized SiO_2 subsequently deposits on the selected substrate. By a reactive sputtering technique, as described, for example, by Amick et al as referenced above, a disk of silicon is bombarded with oxygen ions, which causes vaporization of the silicon, and the vaporized silicon and oxygen ions then react to produce the desired SiO_2. However, these sputtering techniques are similar to the above-described plasma processes in that they frequently impart damage to sensitive devices due to charge bombardment or radiation bombardment of the device. In addition, the films produced by sputtering techniques are often granular, not dense, and not specular (i.e., having good light reflecting properties).

Both the sputtering technique and the plasma-enhanced method for chemical vapor deposition may be used to deposit a dielectric layer which incorporates a selected dopant material. In the former case, an appropriately doped target could be bombarded by selected ions. In the latter case, a dopant-containing material is added to the reactant gases which are then ionized. However, both the above sputtering technique and the above plasma-enhanced method suffer from the difficulties discussed above, particularly that of imparting damage due to charge bombardment or radiation bombardment and plasma-induced heating of the substrate.

Still another known method by which oxide layers may be formed involves thermal processes. In order to form SiO_2, for example, by a thermal process, silane is brought into contact with oxygen at a low temperature and a spontaneous reaction occurs, forming SiO_2. The films formed by thermal processes, however, are usually granular, do not necessarily have good adhesion, and tend to incorporate traps.

It is the alleviation of the prior art problem of imparting damage to sensitive devices due to charge bombardment or radiation bombardment during the formation of an oxide layer thereon to which the present invention is directed.

We have now developed a process of depositing a layer of an oxide of a chosen material on the surface of a selected substrate by low temperature (for example as low as room temperature) photochemical vapor deposition, which process

(i) avoids damage to the substrate from charge- or radiation bombardment,

(ii) minimizes the value of the surface state density at the oxide/substrate interface and thus, in the case of a semiconductor material, minimizes the charge traps in the deposited oxide layer, and

(iii) produces a low density of genera-

tion/recombination centers at the interface between the deposited oxide layer and the substrate and thus provides good minority carrier lifetime in the substrate.

According to the present invention, there is provided a process for forming a layer of an oxide of a chosen material on the surface of a selected substrate, comprising the steps of exposing the substrate to a vapor-phase reactant and an oxygen-containing precursor in the presence of radiation of a predetermined wavelength to photochemically generate neutral oxygen atoms which react with the vapor-phase reactant to form said oxide layer under selected temperature, pressure and flow rate conditions.

In order that the invention may be more fully understood, preferred embodiments of apparatus for carrying out the process will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 illustrates, in schematic form, a preferred apparatus for carrying out the processes according to first and second embodiments of the present invention, in which neutral oxygen atoms are formed by the mercury photosensitized dissociation of an oxygen-containing precursor and are reacted to form an undoped or a doped oxide layer, respectively.

Figure 2 illustrates, in schematic form, a preferred apparatus for carrying out the processes according to third and fourth embodiments of the present invention, in which neutral oxygen atoms are formed by the direct dissociation of an oxygen-containing precursor and are reacted to form an undoped or a doped oxide layer, respectively.

Figure 1 shows, in simplified form, an apparatus suitable for implementation of two process embodiments of the present invention in which neutral oxygen atoms are formed by the mercury photosensitized dissociation of a chemically unreactive oxygen-containing precursor, such as nitrous oxide (N_2O), molecular oxygen (O_2), or nitrogen dioxide (NO_2). (The term "chemically unreactive" is used herein to denote that a substance will not react with the designated reactants under normal mixture conditions). A reaction chamber 10, in which the chemical vapor deposition reaction occurs, is provided with a quartz window 12, which is integral with the top surface of the reaction chamber 10. The quartz window 12 is transmissive to the selected wavelength of radiation used to initiate the desired photochemical reaction to be discussed below, and this radiation 14 of a selected wavelength is produced by the radiation-producing means 16, which may be, for example, an array of low pressure mercury vapor arc lamps. Within the reaction chamber 10, there is a substrate holder 18, which receives a substrate 20 onto which the desired oxide layer is to be deposited.

External to the reaction chamber 10 and adjacent to the bottom surface thereof, there are heating elements 21, which may be formed, for example, of Nichrome wire and are activated by applying a controlled voltage thereto. The heating elements 21 may be used optionally to heat the substrate 20 to the required temperature so that appropriate properties of the deposited layer, such as density, may be obtained. The temperature in the chamber 10 may be maintained as low as room temperature (i.e. 30°C) or as high as required (e.g., 300°C or higher). However, since mercury vapor arc lamps, for example, become less efficient at increased temperatures, it is necessary to provide external water cooling or an external air or nitrogen cooling source to cool these lamps and remove radiant heat produced by the substrate 20 and substrate holder 18 at certain elevated temperatures (as high as 600°C, for example, or higher). For this purpose, the radiation-producing means 16 is completely contained within the enclosure 23, which may be formed of aluminum, and an external cooling means 25, such as pipes with water flowing therethrough as shown in Figure 1 or flowing nitrogen gas, is activated to apply cooling to the enclosure 23. The enclosure 23 is secured to the outside surface of the reaction chamber 10 which surrounds the quartz window 12, but may be removed therefrom as required. Thus, the processing temperature is maintained at a level such that sufficient cooling of the mercury lamps can be accomplished in order to provide efficient lamp performance. The enclosure 23 also provides eye protection to the operator from the radiation 14. Leading from the reaction chamber 10, there is a tube 22 which passes through a valve 24 and then to a vacuum-producing means, such as a pump, (not shown), which is used to evacuate the chamber 10 to a sufficiently low pressure to allow the vapor deposition reaction to occur.

External to the reaction chamber 10, there are chambers 26 and 28 which contain the individual reactant gases for the selected chemical vapor deposition reaction, for example, silane and nitrous oxide. The chambers 26 and 28 are connected to control valves or flowmeters 30 and 32, respectively, which are used to control the amounts of reactants which are introduced into a tube 34. Alternatively, for a second process embodiment of the present invention (discussed below), there are included a third chamber 27, which contains the precursor of the selected dopant material, such as phosphine, and a corresponding control valve or flowmeter 31, which controls the amount of dopant precursor introduced from the chamber 27 into the tube 34, where it is mixed with the other reactant gases discussed above.

The reactant gases flow through the tube 34 into a chamber 36 which contains a pool of mercury (at room temperature) having mercury vapor above it, at a vapor pressure of (10^{-3} Torr) 133.3×10^{-3} Pa at 30°C. The reactant gases thus become mixed with mercury vapor

in the chamber 36 and this reactant gas mixture then passes through a tube 38 and into the reaction chamber 10, where the chemical vapor deposition reaction may be brought about. The components of the apparatus shown in Figure 1 may be constructed of stainless steel or aluminum, unless otherwise specified. The apparatus shown in Figure 1 may be used for either a low pressure continuous flow photochemical reactor system, in which there is a continuous influx of reactant gases and removal of reaction by-products during the photochemical reaction process, or for a static photochemical reactor system, in which specified amounts of reactants are introduced into the reaction chamber, the flow of reactant gases is stopped, and then the photochemical reaction process is allowed to occur.

In practicing the present invention in accordance with the first embodiment thereof, which depends on the photochemical generation of atomic oxygen, and using the apparatus of Figure 1 with only two reactant gas chambers (chambers 26 and 28), a chemical vapor deposition process is performed as generally described by Werner Kern and Richard S. Rosler in the publication entitled, "Advances in Deposition Processes for Passivation Films", in the Journal of Vacuum Science Technology, Vol. 14, No. 5, Sept.—Oct. 1977, pp. 1082—1099, in the discussion of low pressure chemical vapor deposition processes. The reaction chamber 10 is evacuated by the vacuum-producing means to a predetermined pressure, for example 133.3—532.8 Pa (1 to 4 Torr). The selected vapor phase reactant, such as SiH_4, is placed in a chamber such as the chamber 26, and a chemically unreactive oxygen-containing precursor, such as N_2O, is placed in a chamber such as the chamber 28. The valves 30 and 32 are set so that the reactants from the chambers 26 and 28, respectively, in a predetermined ratio and at a predetermined flow rate may pass into the tube 34 and then into the chamber 36, which contains a pool of mercury. These reactant gases become mixed with mercury vapor in the chamber 36 and pass from the chamber 36 through the tube 38 into the reaction chamber 10, which is maintained at approximately room temperature (e.g. 30°C) or up to 200°C or higher. The radiation-producing means 16 is activated and produces the radiation 14 of a selected wavelength required to produce the desired photochemical reaction (e.g. 253.7 nm (2537Å) to produce mercury in an excited state). The radiation 14 passes through the quartz window 12 into the reaction chamber 10, where it excites the mercury (Hg) atoms in the reactant gas mixture to form mercury atoms in an excited state (Hg*) (approximately 5 electron volts above normal ground state, but un-ionized), as shown in Equation (1) below. The Hg* then collides with the oxygen-containing precursor, such as N_2O, and causes the precursor to dissociate and produce atomic oxygen (O), as shown in Equation (2a) below.

In addition, the Hg* may react with the selected vapor phase reactant, such as SiH_4, to produce a reactive radical, such as $\cdot SiH_3$, as shown in equation (2b) below. Finally, the atomic oxygen reacts with the reactant, SiH_4, or the reactive radical, such as $\cdot SiH_3$, to produce the desired oxide, such as SiO and SiO_2, as shown in Equations (3a) and (3b) below. Either SiO or SiO_2 can be produced, depending on the reactant gas ratio of SiH_4 and N_2O (i.e. the steady state concentration of atomic oxygen which oxidizes SiH_4).

(1) $Hg+h\nu\ (2537Å)\rightarrow Hg^*$

where

h=Planck's constant

ν=frequency of absorbed radiation

(2a) $Hg^*+N_2O\rightarrow N_2+O+Hg$

(2b) $SiH_4+Hg^*\rightarrow SiH_3+H\cdot+Hg$

(3a) $SiH_4+O\rightarrow SiO_2+H_2O$ / $\rightarrow SiO+H_2O$

(3b) $\cdot SiH_3+O\rightarrow SiO+H_2O$ / $\rightarrow SiO_2+H_2O$

The reaction of Hg* with SiH_4 to form the radical $\cdot SiH_3$ is a side reaction which is not necessary to the process of the present invention, but leads to the same end product as the major reaction path. The atomic oxygen produced in Equation (2a) above may react directly with the selected vapor phase reactant without first forming an intermediate radical, as described in Equation (3a) above.

Alternatively, the atomic oxygen required for this first process embodiment of the present invention may be formed by the mercury sensitized dissociation of nitrogen dioxide (NO_2) to form atomic oxygen and NO. Further, atomic oxygen may also be formed by the mercury sensitized dissociation of molecular oxygen in accordance with Equations (4) and (5) below, or by other known means for forming atomic oxygen by photochemical processes.

(4) $Hg+h\nu\ (2537Å)\rightarrow Hg^*$

(5) $Hg^*+O_2\rightarrow 2O+Hg$

Since molecular oxygen reacts spontaneously with SiH_4 as discussed in relation to the prior art thermal oxidation process, it is necessary to inhibit this spontaneous thermal oxidation

process in order to permit the formation of atomic oxygen and the reaction thereof with SiH_4 in accordance with the process of the present invention. This inhibition is accomplished by carefully controlling the operating pressure and the ratio of reactant gases, as discussed in more detail in Example 3 below. By controlling such process parameters the thermal oxidation process may be completely inhibited and the oxidation process of the present invention may occur without any competing processes.

By the above-described process of the present invention, oxygen atoms are produced by a photochemical process which generates only neutral particles. Thus, the prior art problems associated with the generation of charged particles and high energy radiation which bombard the substrate have been avoided. The value of the surface state density (N_{ss}) at the oxide/semiconductor substrate interface and thus the charge traps in the oxide or insulator layer are minimized by the process of the present invention. In addition, a low density of generation/recombination centers (i.e., dangling bonds or traps) is produced at the interface between the deposited oxide and the substrate and thus good minority carrier lifetime in the substrate is achieved in devices formed by the process of the present innvention. In addition, the process of the present invention provides enhanced protection against device damage due to radiation (i.e. from a cobalt-60 source) by minimizing the creation of dangling bonds and traps during the deposition of the oxide or insulator layer. These traps and dangling bonds normally increase the probability of radiation damage to the device and their minimization thus reduces the probability of radiation damage. Further, the problem of boundary migration has been eliminated since the process of the present invention can be conducted at a relatively low temperature, i.e. as low as room temperature, and the associated problem of decreased device yield encountered in the high temperature fabrication of high density devices such as very large scale integrated circuits and very high speed integrated circuits, has been avoided. In addition, the prior art problem of plasma-induced heating is avoided by the process of the present invention since selective absorption of radiation by the substrate does not occur in the process described herein. Furthermore, the process of the present invention is free of particulate formation, for example, on chamber walls, which is a problem often encountered in the prior art processes discussed above. Finally, the oxide layer formed by the process of the present invention is dense, non-granular, scratch-resistant, specular, has negligible porosity, and is strongly adherent to a variety of surfaces, such as semiconductor, metal and inorganic surfaces. Such oxide layers find utility both as a passivation layer and as a gate insulator layer in integrated circuit devices. Furthermore, these oxide layers may be used as a conformal coating on integrated circuits and hybrid microcircuits. In addition, these oxide layers may be used in the fabrication of HgCdTe photoconductive and photovoltaic devices. This first process embodiment of the present invention and the related third process embodiment discussed below are, to my knowledge, the first demonstration of the use of a photochemical process for the deposition of a dielectric oxide layer on a substrate.

Using the above-described process, the present invention may also be used to oxidize trimethyl aluminum, $(CH_3)_3Al$, to Al_2O_3; trimethyl gallium, $(CH_3)_3Ga$, to Ga_2O_3; germane, GeH_4, to GeO_2; diborane, B_2H_6, to B_2O_3; trimethyl indium, $(CH_3)_3In$ to In_2O_3; titanium tetrachloride, $TiCl_4$, to TiO_2; tungsten hexafluoride, WF_6, to W_2O_3, and hafnium hydride, HfH_4, to HfO_2. This first process embodiment of the present invention is illustrated in Example 1 below.

Furthermore, a process carried out in accordance with a second embodiment of the present invention may be performed by practicing the present invention as described above, using the apparatus of Figure 1 with three (3) reactant gas chambers (chambers 26, 27, and 28), to deposit on the surface of a chosen substrate an oxide layer which incorporates a selected dopant material in order to modify the physical, electrical, or optical characteristics of the oxide layer. To accomplish this second process embodiment of the present invention, the selected vapor phase reactant, such as SiH_4, is exposed to simultaneously formed and photochemically generated neutral oxygen atoms and neutral atoms or atomic fragments of the selected dopant, such as phosphorus-containing phosphinyl radicals. The neutral atomic particles are produced by the mercury photosensitized dissociation of a chemically unreactive oxygen-containing precursor, such as nitrous oxide (N_2O) and a chemically unreactive dopant-containing precursor, such as phosphine (PH_3), which results in the generation of atomic oxygen and neutral phosphinyl radicals, respectively, as shown in Equations (6) through (8) below. The atomic oxygen and phosphinyl radicals subsequently oxidize the SiH_4 to phosphorus-doped silicon dioxide [$Si(P)O_2$], as shown in Equation (9) below.

(6) $Hg+h\nu\ (2537Å) \rightarrow Hg^*$

(7) $Hg^*+N_2O \rightarrow N_2+O+Hg$

(8) $Hg^*+PH_3 \rightarrow PH_2+H\cdot+Hg$

(9) $SiH_4+O+\cdot PH_2 \rightarrow Si(P)O_2+H_2O$

A mechanistic alternative to the sequence described above involves the simultaneous oxidation of both SiH_4 and PH_3 by atomic

oxygen, as indicated in Equations (10) through (12) below. Thus, atomic oxygen alone may be sufficient to bring about the desired reaction as shown in Equation (12) below. Consequently, the production of neutral particles of the selected dopant material as described above in Equation (8) may not be necessary in practicing the second process embodiment of this invention, but may occur.

(10) $Hg+h\nu\ (2537Å)\rightarrow Hg^*$

(11) $Hg^*+N_2O\rightarrow N_2+O+Hg$

(12) $SiH_4+PH_3+O\rightarrow Si(P)O_2+H_2O$

The procedure followed to accomplish this second process embodiment of the invention is essentially as described above with respect to the first process embodiment of the present invention, except that additionally, a controlled amount of a selected dopant-containing precursor is introduced from the chamber 27 through the control valve 31 into the tube 34, where it mixes with the reactant gases from the chambers 26 and 28.

Thus, by this second process embodiment of the present invention, a doped dielectric film may be deposited by a low-temperature process which avoids the generation of charged particles and high energy radiation and their consequent bombardment damage to the substrate. Additionally, this embodiment has all the advantages enumerated above with respect to the formation of an undoped dielectric layer by the process of the present invention. This second process embodiment of the present invention and the related fourth process embodiment discussed below are, to my knowledge, the first demonstration of the use of a photochemical process for the deposition of a doped dielectric layer.

By the process according to this second embodiment of the present invention, other dopants besides phosphorus may be incorporated in the deposited dielectric layer by addition of the corresponding dopant-containing precursor to the reactant gas mixture. For example, diborane (B_2H_6) may be used for boron doping; arsine (AsH_3) may be used for arsenic doping, stibine (SbH_3) may be used for antimony doping, hydrogen selenide (H_2Se) may be used for selenium doping, hydrogen sulfide (H_2S) may be used for sulfur doping, or hydrogen telluride (H_2Te) may be used for tellurium doping. Other dopant-containing precursors which are capable of the mercury photosensitized dissociation reaction of the type discussed herein may also be used. Other dielectric films besides SiO_2 may be formed, as discussed above. This second process embodiment of the present invention is illustrated in more detail in Example 2 below.

Turning now to Figure 2, there is shown an apparatus suitable for implementation of the processes according to of third and fourth embodiments of the present invention, in which neutral oxygen atoms are formed by a direct photochemical reaction of an oxygen-containing precursor, thus eliminating the requirement of mercury photosensitization. A reaction chamber 40 in which the photochemical vapor deposition reaction occurs is provided with a transparent window 42, which is integral with the top surface of the chamber 40. The material of which the window 42 is formed is chosen to be transparent to the selected wavelength of radiation which will be used for the photochemical reaction. Radiation 44 having a selected wavelength is produced by a radiation-producing means 46, such as an array of low pressure mercury vapor arc lamps, and passes through the window 42 into the chamber 40. Within the reaction chamber 40, there is a substrate holder 48, which holds a substrate 50 onto which the desired oxide layer is to be deposited. External to the reaction chamber 40 at the bottom surface thereof, there are heating elements 51, which may be formed of Nichrome (Registered Trade Mark) wire and are activated by application of a controlled voltage thereto. The heating elements 51 may be used optionally to preheat the substrate 50 to the required temperature for forming a deposited layer with desired properties.

In practicing the present invention, the temperature in the chamber 40 may be maintained as low as room temperature or as high as 200°C or higher. In order to provide the required cooling of the radiation-producing means 46, as previously discussed in relation to Figure 1, radiation-producing means 46 is completely enclosed within the enclosure 53, which may be formed of aluminum, and an external cooling means 55, such as pipes with water flowing therethrough as shown in Figure 2 or flowing nitrogen gas, is activated to applying cooling to the enclosure 53. The enclosure 53 performs the additional function of eliminating the formation of ozone which would occur if the radiation 44 (such as 184.9 nm (1849Å) radiation) were allowed to contact molecular oxygen in the open atmosphere, which would cause the formation of atomic oxygen that would then react with additional molecular oxygen in the atmosphere to form ozone. The enclosure 53 is secured to the outside surface of the reaction chamber 40 which surrounds the quartz window 42, but may be removed therefrom as required.

Leading from the reaction chamber 40, there is a tube 52 which passes through a valve 54 and then to a vacuum producing means, e.g., a vacuum pump, (not shown) which is used to evacuate the chamber 40 to a sufficiently low pressure (e.g., 133.3—533.2 Pa (1—4 Torr)) to allow the vapor deposition reaction to occur.

External to the reaction chamber 40, there are chambers 56 and 58, which contain the

individual selected reactant gases, such as silane (SiH_4) and nitrous oxide (N_2O), respectively, for producing the desired photochemical reaction. The chambers 56 and 58 are connected to control valves or flowmeters 60 and 62, respectively, which are used to control the amounts of reactants which are introduced into a tube 64. Alternatively, in accordance with a fourth process embodiment of the present invention (discussed below), there are included a third chamber 57, which contains the precursor of the selected dopant material, such as phosphine, and a corresponding control valve or flowmeter 61, which controls the amount of dopant precursor introduced from the chamber 57 into the tube 64, where it is mixed with the other reactant gases discussed above. The reactant gases flow through the tube 64 into the reaction chamber 40, where the photochemical reaction may be brought about. The components of the apparatus shown in Figure 2 may be constructed of stainless steel or aluminum, unless otherwise specified. The apparatus shown in Figure 2 may be used for either a continuous flow photochemical reactor system or a static photochemical reactor system, as discussed above with reference to Figure 1.

In practicing the present invention in accordance with the third embodiment thereof and using the apparatus of Figure 2, the general process described in relation to the first process embodiment of Figure 1 is followed, except that no mercury is used for photosensitization. The valves 60 and 62 are set so that the reactant gases, such as SiH_4 and N_2O, from the chambers 56 and 58, respectively, pass in a predetermined ratio and at a predetermined flow rate into the tube 64 and then into the reaction chamber 40. The radiation-producing means 46 is activated and produces the radiation 44 of a selected wavelength, which is the appropriate wavelength to cause the direct dissociation of the selected oxygen-containing precursor (e.g. 175.0—195.0 nm (1750—1950Å) for N_2O). The radiation 44 passes through the window 42, which is formed of a material that is transparent to the wavelength of the radiation 44. The radiation 44 passes into the reaction chamber 40, where it causes the dissociation of the selected oxygen-containing precursor, such as N_2O, into atomic oxygen, which then reacts with the selected vapor phase reactant, such as SiH_4, to form the desired oxide, such as SiO_2 and SiO, as shown in Equations (13) and (14) below.

(13) $N_2O+h\nu$ (1849Å)$\rightarrow O+N_2$

(14) $SiH_4+O \rightarrow SiO_2+H_2O$ or $SiH_4+O \rightarrow SiO+H_2O$

Alternatively, the atomic oxygen required for this third process embodiment of the present invention may be formed by the direct photochemical dissociation of molecular oxygen as shown in Equation (15) below or of nitrogen dioxide (NO_2) as shown in Equation (16) below or of similar known materials which are capable of dissociation to oxygen by a direct photochemical process.

(15) $O_2+h\nu$ (184.9 nm (1849Å))$\rightarrow 2O$

(16) $NO_2+h\nu$ (350—600 nm (3500—6000Å))$\rightarrow O+NO$

When molecular oxygen is used as the source of atomic oxygen, the operating pressure and reactant gas ratio must be carefully controlled in order to inhibit the spontaneous thermal oxidation of the SiH_4 by the O_2, as previously discussed in relation to an alternative process embodiment of the present invention and as illustrated in Example 3 below.

By the above-described process in accordance with this third embodiment of the present invention, oxygen atoms are generated by a photochemical process which produces only neutral particles. Thus, the previously-discussed prior art problems caused by the generation of charged particles and high energy radiation and their bombardment of the substrate have been avoided. The advantages of this third process embodiment of the present invention are the same as those discussed in relation to the first process embodiment described with respect to Figure 1. In addition, the process according to this third embodiment has the advantage that no photosensitizing mercury is necessary, and thus possible mercury contamination of the deposited oxide can be avoided. Further, the apparatus for carrying out the process according to this third embodiment is less complex than an apparatus requiring the use of mercury.

Using the above-described process, the present invention may also be used to deposit dielectric oxides of gallium, germanium, boron, and indium and metal oxides of aluminum, tungsten, titanium, and hafnium, using the gas phase reactants discussed in relation to Figure 1. This third process embodiment of the present invention is illustrated in Example 3 below.

Furthermore, a process carried out in accordance with a fourth embodiment of the present invention may be performed by practicing the present invention as described above, but also using the apparatus of Figure 2 with three (3) reactant gas chambers (chambers 56, 57, and 58), to deposit an oxide layer which incorporates a selected dopant material, on the surface of a chosen substrate. To accomplish this fourth process embodiment of the present invention, the selected vapor phase reactant, such as SiH_4, is exposed to photochemically generated neutral oxygen atoms in the presence of a dopant-containing precursor, such as

phosphine (PH_3). The neutral atomic oxygen is produced by direct dissociation of an oxygen-containing precursor, such as N_2O, by radiation of a selected wavelength as shown in Equation (17) below. The atomic oxygen then simultaneously oxidizes the SiH_4 and PH_3 to form the desired phosphorus-doped SiO_2 as shown in Equation (18) below.

(17) $N_2O+h\nu$ (184.9 nm (1849Å)$\rightarrow O+N_2$

(18) $SiH_4+PH_3+O\rightarrow Si(P)O_2+H_2O$

A possible alternative to the above-described sequence involves the direct dissociation of the dopant-containing precursor such as phospine to form a neutral phosphinyl radical as shown in Equation (19) below. The phosphinyl radical so formed and the atomic oxygen formed in accordance with the direct dissociation reaction of equation (17) above then react with the silane reactant to form the desired phosphorus-doped SiO_2 as shown in Equation (20) below.

(19) $PH_3+h\nu$ (1849Å)$\rightarrow \cdot PH_2+H\cdot$

(20) $SiH_4+O+\cdot PH_2\rightarrow Si(P)O_2+H_2O$

The procedure followed to accomplish the process according to the fourth embodiment of this invention is essentially as described above with respect to the third process embodiment of the present invention, except that additionally a controlled amount of a selected dopant-containing precursor, such as phosphine gas, is introduced from the chamber 57 and through the valve 61 into the tube 64, where it mixes with the reactant gases from the chambers 56 and 58.

Thus, by this fourth process embodiment of the present invention, a doped dielectric film may be deposited by a low-temperature process which avoids the generation of charged particles and high energy radiation and their consequent bombardment damage to the substrate and additionally avoids the use of mercury for photosensitization. The significance of these advantages has been discussed above with respect to the third process embodiment of the present invention. Various dopant materials other than phosphine may be used, and these materials include diborane, arsine, stibine, hydrogen selenide, hydrogen sulfide, hydrogen telluride, or other dopant-containing precursors which are capable of simultaneous oxidation by atomic oxygen with the selected gas phase reactant to form the desired doped oxide layer. This fourth process embodiment of the present invention is illustrated in Example 4 below.

Example 1

This example illustrates the use of the process according to the first embodiment of the present invention as previously described herein.

Using the apparatus described and illustrated in relation to Figure 1 with two reactant gas chambers, SiO and SiO_2 were independently deposited on the surface of a wafer of silicon having a 5.08 cm (two-inch) diameter. Nitrous oxide was used as the oxygen-containing precursor and silane was the selected vapor phase reactant. The reaction chamber 10 was evacuated by the vacuum-producing means to a pressure of 133.3×10^{-3} Pa (10^{-3} Torr), then back-filled with nitrogen, and again evacuated to a pressure of 133.3×10^{-3} Pa (10^{-3} Torr). The flowmeters 30 and 32 were activated to admit the reactant gases (SiH_4 and N_2O) in a predetermined ratio into the tube 34 and subsequently into the chamber 36 and the reaction chamber 10, and the reactant gas flow rates were stabilized. The operating pressure within the reaction chamber 10 was adjusted by means of the valve 24 to achieve a pressure of approximately 133.3 Pa (1 Torr). The heating elements 21 and the cooling means 25 were activated. Finally, the low pressure mercury arc resonance lamps were activated and emitted radiation at 253.7 nm (2537Å), which was absorbed by the mercury vapor in the reaction chamber, producing photo-excited mercury atoms, which collided with the nitrous oxide to form atomic oxygen. The atomic oxygen then oxidized the silane to either SiO_2 or SiO. When using a continuous flow photochemical reactor system at an operating pressure of 266.6 Pa (2 Torr), with a reactant gas flow rates of 2 standard cubic centimeters per minute (sccm) of SiH_4 and 50 sccm of N_2O, a layer of SiO_2 was produced. When reactant gas flow rates of 2 sccm of SiH_4 and 10 sccm of N_2O were used in a continuous flow system, a layer of SiO was produced. At a substrate temperature of 100°C, the silicon oxide layer was deposited at the rate of 20 nm (200Å) per minute using a continuous flow system. When using a static photochemical reactor system with reactant gas pressures of SiH_4 and N_2O equivalent to 3 mm and 12 mm, silicon monoxide (SiO) was produced as a layer on the surface of the silicon wafer. When reactant gas pressures of SiH_4 and N_2O of 3.0 mm to 30 mm Hg respectively were used in a static system, silicon dioxide (SiO_2) was produced as the layer on the silicon wafer.

The refractive index of the photodeposited silicon oxide layers formed by the process of this embodiment of the present invention was determined by ellipsometry as a function of the reactant gas mixture ratio, N_2O/SiH_4. Mixtures rich in N_2O (i.e. atomic oxygen) produced films with a refractive index characteristic of SiO_2, i.e. 1.45. Mixtures of N_2O/SiH_4 progressively leaner in N_2O yielded silicon oxide films with less oxygen content and, ultimately, SiO with a refractive index of 1.88. The etch rate

characteristics of the photodeposited SiO_2 material in buffered HF were comparable to those of SiO_2 films deposited by low temperature plasma techniques. The stoichiometric composition of the film was determined by Auger electron spectroscopy. The SiO_2 films exhibited an excellent composition/depth profile and stoichiometrically were equivalent to pure SiO_2. The SiO films exhibited slower etch rates than the SiO_2 films due to the depleted oxygen content of the SiO films, which was confirmed by Auger spectroscopic analysis. The breakdown voltage of the SiO_2 films formed by the process of the present invention was determined to be 3.0×10^6 volts/centimeter, the dielectric constant was approximately 5.5, and the dissipation factor was 1.5×10^{-2}, which measurements are comparable to the values obtained for similar films formed by a prior art thermal process previously discussed. The density of the SiO_2 films formed by the process of the present invention was 2.3 grams/cubic centimeter.

The photochemically deposited SiO_2 layers formed by the above-described process of the present invention have application as dielectric layers for the passivation of semiconductor devices, particularly charge-sensitive microelectronic devices, such as silicon MOS devices, HgCdTe photoconductive and photovoltaic devices, and GaAs field-effect transistors. These layers may be deposited to a typical thickness of 120—150 nm (1200—1500Å) for such a purpose. In addition, the process of the present invention may be used to deposit an anti-reflective oxide coating on a lens, including a plastic lens, or a solar cell, or to deposit a protective oxide coating on a mirror.

Using the above-described process, SiO_2 layers were similarly deposited on Ge, InSb, and Al substrates.

Example 2

This example illustrates the use of the process according to the second embodiment of the present invention as previously described herein.

Using the apparatus described and illustrated in relation to Figure 1 with three reactant gas chambers, a layer of phosphorus-doped SiO_2 was deposited on the surface of a silicon wafer having a 5.08 cm (two-inch) diameter. The general procedure described in relation to Example 1 above was followed, with the addition of a third reactant gas. Nitrous oxide was used as the oxygen-containing precursor, silane was the selected vapor phase reactant, and phosphine was the phosphorus dopant-containing precursor. The process was initiated by the photochemical excitation of mercury vapor at 133.3×10^{-3}Pa (10^{-3} Torr) in a quartz reaction chamber. Low pressure mercury arc resonance lamps emitted radiation at 253.7 nm (2537Å), which was absorbed by the mercury vapor in the reaction chamber, producing photo-excited mercury atoms that reacted with the N_2O and PH_3 as shown in Equations (7) and (8) discussed above. The atomic oxygen and neutral phosphinyl radical ($\cdot PH_2$) thus formed reacted with the SiH_4 to form phosphorus-doped silicon dioxide [$Si(P)O_2$] as shown in Equation (9) discussed above, which deposited as a layer on the silicon wafer. Using a continuous flow photochemical reactor system, with a reactant gas flow rates of SiH_4, N_2O, and PH_3 of 2, 60 and 1 sccm respectively, a phosphorus-doped SiO_2 layer was deposited on the substrate at the rate of 200Å/minute and the phosphorus content of the deposited layer was approximately 5%. In addition, a low pressure static photochemical reactor system was used with a reactant gas pressures of SiH_4, N_2O and PH_3 equivalent to 3, 30 and 1 mm of Hg respectively. The phosphorus-doped SiO_2 layer was deposited at initial rates of 20 nm/minute (200Å/minute) and the phosphorus-content in the deposited layer was approximately 5%. Using a reactant gas pressures of SiH_4, N_2O and PH_3 equivalent to 2, 30 and 12 mm Hg respectively in a static system, levels of phosphorus-doping of 17% in the deposited layer have been achieved.

The refractive index of the photodeposited phosphorus-doped SiO_2 layer was dependent on the N_2O/PH_3 ratio and indices from 1.55 to 1.65 were measured. The films exhibiting the higher refractive indices indicated a greater phosphorus doping content of the SiO_2 dielectric material. The chemical composition of the phosphorus-doped SiO_2 films was determined by Auger electron spectroscopy and the phosphorus content was confirmed by energy dispensive X-ray analysis (EDAX). The etch rate in "P-etch" [i.e., a mixture of 60 milliliters (ml) of water, 3 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 films was significantly faster than that of pure SiO_2, yielding values of 20 nm/second (200Å/second), which concur with values of phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed. The amount of dopant contained in the dielectric layer deposited by the above-described process may be controlled by adjusting the amount of dopant-containing precursor which is added to the reactant gas mixture.

Although phosphorus-doped SiO_2 layers were formed as described above, it is also possible to form phosphorus-doped SiO layers by this process embodiment of the present invention by increasing the ratio of SiH_4 to N_2O in a manner similar to that described in Example 1.

The photochemically deposited phosphorus-doped SiO_2 films formed by the above-described process of the present invention have application as dielectric layers for the passivation of charge-sensitive microelectronic devices, such as silicon MOS devices. In addition, these phosphorus-doped films may be

used as a counter-diffusion layer on GaAs devices for the minimization of out-diffusion of both gallium (Ga) and arsenic (As) at temperatures exceeding 100°C.

Example 3

This example illustrates the use of the process in accordance with the third embodiment of the present invention as previously described herein.

Using the apparatus shown in Figure 2 with two reactant gas chambers, a layer of SiO_2 was deposited on the surface of a wafer of silicon having a 5.08 cm (two-inch) diameter. The general procedure described in relation to Example 1 above was followed, except that mercury sensitization was not used. A continuous flow photochemical reactor system was used. The oxygen-containing precursor was N_2O and the selected vapor phase reactant was SiH_4. Radiation having a wavelength of 1849Å was used to dissociate the N_2O; and the window of the reaction chamber was formed of "spectrasil" (obtained from Thermal American Fused Quartz, Montville, New Jersey), which was transparent to 1849Å radiation. Low pressure mercury arc lamps designed with "spectrasil" envelopes emitted radiation at 1849Å, which was transmitted through the "spectrasil" window into the reaction chamber. The radiation was absorbed by the N_2O and caused dissociation thereof to produce atomic oxygen. The atomic oxygen then reacted with the SiH_4 to produce the desired SiO_2 which deposited as a layer on the silicon wafer. A reactant gas flow rates of SiH_4 and N_2O of 2 sccm and 60 sccm respectively and an operating pressure of 493.2 Pa (3,7 Torr) were used. The SiO_2 layer was deposited at the rate of 70 nm (700Å) in 30 minutes, and even higher rates may be achieved with process optimization.

The refractive index of the photodeposited SiO_2 layer formed by the above-described process of the present invention was determined by ellipsometry and the films were found to have a refractive index characteristic of SiO_2, i.e. 1.45. The etch rate characteristics of the photodeposited SiO_2 material in buffered HF were comparable to those of SiO_2 films deposited by low temperature plasma techniques.

Although SiO_2 layers were formed as described above, it is also possible to form SiO layers by this process embodiment of the present invention by increasing the ratio of SiH_4 to N_2O in a manner similar to that described in Example 1.

The photochemically deposited SiO_2 layers formed by the above-described process of the present invention have application as dielectric layers for the passivation of semiconductor devices, particularly charge sensitive microelectronic devices, such as MOS devices and GaAs, HgCdTe photoconductive and photovoltaic devices, field-effect transistors. In addition, the oxide layers formed by the above-described process may be used on electro-optical materials such as lenses and mirrors or on solar cells as described in relation to Example 1.

Using the above-described process, SiO_2 layers were similarly deposited on Ge, InSb, and Al substrates.

Furthermore, using the general process described above, a layer of SiO_2 was deposited on the surface of a silicon wafer, using molecular oxygen (O_2) as the oxygen-containing precursor. In order to completely inhibit the spontaneous thermal oxidation reaction of O_2 and SiH_4, a nitrogen gas diluent was used and the pressure and flow rate conditions of the reactant gases were carefully controlled. Using an operating pressure of 0—666.5 Pa (0—5 Torr) and a reactant gas flow rates of SiH_4, O_2 and N_2 of 1, 20 and 80 sccm, a layer of SiO_2 was deposited at the rate of 300—400 nm (3000 to 4000Å) in 30 minutes. Thus, it may be seen that the use of molecular oxygen as the oxygen-containing precursor in practicing the present invention greatly enhances the oxide deposition rate.

Example 4

This example illustrates the use of the process in accordance with the fourth embodiment of the present invention as previously described herein.

Using the apparatus described and illustrated in relation to Figure 2 with three reactant gas chambers, a phosphorus-doped SiO_2 layer was deposited on the surface of a silicon wafer having a 5.08 cm (two-inch) diameter. The general procedure described in relation to Example 3 above was followed, with the addition of a third reactant gas. A continuous flow photochemical reactor system was used. Nitrous oxide was used as the oxygen-containing precursor, silane was the selected vapor phase reactant, and phosphine was the dopant-containing precursor. Radiation having a wavelength of 184.9 nm (1849Å) was used to dissociate the N_2O and the window of the reaction chamber was formed of "spectrasil" as discussed in relation to Example 3. The 184.9 nm (1849Å) radiation was absorbed by the N_2O and caused dissociation thereof to produce atomic oxygen. The atomic oxygen then reacted with the SiH_4 and PH_3 as shown in Equation (18) above, to produce the desired phosphorus-doped SiO_2, which deposited as a layer on the silicon wafer. A low pressure continuous flow photochemical reactor system was used with a reactant gas flow rates of SiH_4, N_2O, and PH_3 of 2, 60 and 4 sccm respectively. The SiO_2 was deposited at the rate of 33 nm (330Å) in 30 minutes, and even higher rates may be achieved with process optimization. The phosphorus-content of the deposited layer was approximately 5%.

The refractive index of the photodeposited

phosphorus-doped SiO_2 layer formed as described above was 1.75. The chemical composition of the deposited film was determined by Auger electron spectroscopy to be the value discussed above. The etch rate in "P-etch" [i.e., a mixture of 60 ml of water, 30 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 film was determined to be significantly faster than that of pure SiO_2, having values comparable to phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed.

The photochemically deposited phosphorus-doped SiO_2 films formed by the above-described process of the present invention find utility as discussed in relation to Example 2.

While the present invention has been particularly described with the respect to the preferred embodiments thereof, it will recognized by those skilled in the art that certain modifications in form and detail may be made without departing from the scope of the invention. In particular, the scope of the invention is not limited to the photochemical vapor deposition of silicon oxides, but is intended to include the photochemical vapor deposition of an oxide of any gas phase reactant that will react with atomic oxygen, such as reactants containing germanium, gallium, boron, indium, aluminum, titanium, tungsten and hafnium. In addition, the chemically unreactive oxygen-containing precursor is not limited to nitrous oxide, molecular oxygen, or nitrogen dioxide, but is intended to include any material which will photochemically dissociate to atomic oxygen, either with or without mercury sensitization. Further, the substrate on which oxide deposition may be performed by the process of the present invention is not limited to silicon which was used merely as an example, but may include other semiconductor substrate materials, such as GaAs, HgCdTe, or InSb, or electro-optical materials, such as lenses or mirrors, or GaAs or Si solar cells. Finally, the scope of the invention is not limited to the use of phosphine to produce phosphorus-doping, but is intended to include any dopant-containing precursor which is capable of mercury photosensitized dissociation to form neutral particles or which is capable of simultaneous oxidation by atomic oxygen with the selected gas reactant. Such precursors include diborane, arsine, stibine, hydrogen selenide, hydrogen sulfide, or hydrogen telluride, to produce boron-, arsenic-, antimony-, selenium-, sulfur-, or tellurium-doping, respectively.

Claims

1. A process for forming a layer of an oxide of a chosen material on the surface of a selected substrate comprising the steps of exposing the substrate to a vapor-phase reactant and a chemically unreactive gaseous oxygencontaining precursor in the presence of radiation of a predetermined wavelength which produces dissociation of the oxygen-containing precursor to generate neutral oxygen atoms that react with the vapor-phase reactant to form the oxide layer on the surface of the substrate under selected temperature, pressure and flow rate conditions.

2. A process according to claim 1, wherein said vapor-phase reactant contains silicon, germanium, gallium, boron, indium, aluminum, titanium, tungsten, or hafnium.

3. A process according to claim 2, wherein said vapor-phase reactant is silane (SiH_4) and said oxide is silicon dioxide and/or silicon monoxide.

4. A process according to any preceding claim, wherein said oxygen-containing precursor is nitrous oxide (N_2O), nitrogen dioxide (NO_2), or molecular oxygen (O_2) under selected pressure and flow rate conditions.

5. A process according to any preceding claim, wherein the oxide layer is formed in the presence of a gaseous dopant-containing material to incorporate dopant atoms into said oxide.

6. A process according to any preceding claim, wherein mercury vapor is added to said reactant and said precursor to cause mercury photosensitized dissociation of a chosen oxygen-containing precursor.

7. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a static photochemical reactor whereby the SiH_4 is present at a pressure equivalent to 399.9 Pa (3 millimeters of mercury) and the N_2O is present at a pressure equivalent to 1599.6 Pa (12 millimeters of mercury), the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon monoxide.

8. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a continuous flow photochemical reactor whereby the SiH_4 has a gas flow rate of 2 standard cubic centimeters per minute and the N_2O has a gas flow rate of 10 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon monoxide.

9. A process according to any of the claims 1—5, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the predetermined wavelength is 175—195 nm (1750 to 1950Å), the SiH_4 has a gas flow rate of 2 standard cubic centimeters per minute, and the N_2O has a gas flow rate of 50 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide (SiO_2).

10. A process according to any of the claims 1—5, wherein the oxygen-containing pre-

phosphorus-doped SiO_2 layer formed as described above was 1.75. The chemical composition of the deposited film was determined by Auger electron spectroscopy to be the value discussed above. The etch rate in "P-etch" [i.e., a mixture of 60 ml of water, 30 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 film was determined to be significantly faster than that of pure SiO_2, having values comparable to phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed.

The photochemically deposited phosphorus-doped SiO_2 films formed by the above-described process of the present invention find utility as discussed in relation to Example 2.

While the present invention has been particularly described with the respect to the preferred embodiments thereof, it will recognized by those skilled in the art that certain modifications in form and detail may be made without departing from the scope of the invention. In particular, the scope of the invention is not limited to the photochemical vapor deposition of silicon oxides, but is intended to include the photochemical vapor deposition of an oxide of any gas phase reactant that will react with atomic oxygen, such as reactants containing germanium, gallium, boron, indium, aluminum, titanium, tungsten and hafnium. In addition, the chemically unreactive oxygen-containing precursor is not limited to nitrous oxide, molecular oxygen, or nitrogen dioxide, but is intended to include any material which will photochemically dissociate to atomic oxygen, either with or without mercury sensitization. Further, the substrate on which oxide deposition may be performed by the process of the present invention is not limited to silicon which was used merely as an example, but may include other semiconductor substrate materials, such as GaAs, HgCdTe, or InSb, or electro-optical materials, such as lenses or mirrors, or GaAs or Si solar cells. Finally, the scope of the invention is not limited to the use of phosphine to produce phosphorus-doping, but is intended to include any dopant-containing precursor which is capable of mercury photosensitized dissociation to form neutral particles or which is capable of simultaneous oxidation by atomic oxygen with the selected gas reactant. Such precursors include diborane, arsine, stibine, hydrogen selenide, hydrogen sulfide, or hydrogen telluride, to produce boron-, arsenic-, antimony-, selenium-, sulfur-, or tellurium-doping, respectively.

Claims

1. A process for forming a layer of an oxide of a chosen material on the surface of a selected substrate comprising the steps of exposing the substrate to a vapor-phase reactant and a chemically unreactive gaseous oxygencontaining precursor in the presence of radiation of a predetermined wavelength which produces dissociation of the oxygen-containing precursor to generate neutral oxygen atoms that react with the vapor-phase reactant to form the oxide layer on the surface of the substrate under selected temperature, pressure and flow rate conditions.

2. A process according to claim 1, wherein said vapor-phase reactant contains silicon, germanium, gallium, boron, indium, aluminum, titanium, tungsten, or hafnium.

3. A process according to claim 2, wherein said vapor-phase reactant is silane (SiH_4) and said oxide is silicon dioxide and/or silicon monoxide.

4. A process according to any preceding claim, wherein said oxygen-containing precursor is nitrous oxide (N_2O), nitrogen dioxide (NO_2), or molecular oxygen (O_2) under selected pressure and flow rate conditions.

5. A process according to any preceding claim, wherein the oxide layer is formed in the presence of a gaseous dopant-containing material to incorporate dopant atoms into said oxide.

6. A process according to any preceding claim, wherein mercury vapor is added to said reactant and said precursor to cause mercury photosensitized dissociation of a chosen oxygen-containing precursor.

7. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a static photochemical reactor whereby the SiH_4 is present at a pressure equivalent to 399.9 Pa (3 millimeters of mercury) and the N_2O is present at a pressure equivalent to 1599.6 Pa (12 millimeters of mercury), the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon monoxide.

8. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a continuous flow photochemical reactor whereby the SiH_4 has a gas flow rate of 2 standard cubic centimeters per minute and the N_2O has a gas flow rate of 10 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon monoxide.

9. A process according to any of the claims 1—5, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the predetermined wavelength is 175—195 nm (1750 to 1950Å), the SiH_4 has a gas flow rate of 2 standard cubic centimeters per minute, and the N_2O has a gas flow rate of 50 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide (SiO_2).

10. A process according to any of the claims 1—5, wherein the oxygen-containing pre-

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cursor is molecular oxygen (O_2) and nitrogen (N_2) is admixed thereto, said predetermined wavelength is 184.9 nm (1849Å), the vapor-phase reactant is silane (SiH_4), said pressure is 0—666.5 Pa (0 to 5 millimeters) of mercury, the gas flow rates of the SiH_4, O_2, and N_2 are 1, 20, and 80 standard cubic centimeters per minutes, respectively, and the oxide is silicon dioxide.

11. A process according to claim 5 or 6, wherein the dopant-containing material is phosphine (PH_3), diborane (B_2H_6), arsine (AsH_3), stibine (SbH_3), hydrogen selenide (H_2Se), hydrogen sulfide (H_2S), or hydrogen telluride (H_2Te).

12. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the predetermined wavelength is 253.7 nm (2537Å), the gas flow rates of the SiH_4 and N_2O are 2 and 50 standard cubic centimeters per minute, respectively, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide.

Revendications

1. Procédé pour former une couche d'un oxyde d'un matière choisie sur la surface d'un substrat sélectionné, comprenant les étapes qui consistent à exposer le substrat à un réactif en phase vapeur et à un précurseur contenant de l'oxygène gazeux, chimiquement non réactif, en présence d'un rayonnement d'une longueur d'onde prédéterminée qui produit une dissociation du précurseur contenant de l'oxygène pour donner des atomes d'oxygène neutres qui réagissent avec le réactif en phase vapeur pour former la couche d'oxyde sur la surface du substrat, dans des conditions sélectionnées de température, de pression et de débit d'écoulement.

2. Procédé selon la revendication 1, dans lequel ledit réactif en phase vapeur contient du silicium, du germanium, du gallium, du bore, de l'indium, de l'aluminium, du titane, du tungstène ou de l'hafnium.

3. Procédé selon la revendication 2, dans lequel ledit réactif en phase vapeur est un silane (SiH_4) et ledit oxyde est du bioxyde de silicium et/ou du monoxyde de silicium.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit précurseur contenant de l'oxygène est du protoxyde d'azote (N_2O), du peroxyde d'azote (NO_2) ou de l'oxygène moléculaire (O_2) dans des conditions sélectionnées de pression et de débit d'écoulement.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la couche d'oxyde est formée en présence d'une matière gazeuse contenant un dope pour introduire des atomes de dope dans ledit oxyde.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel de la vapeur de mercure est additionnée audit réactif et audit précurseur pour provoquer une dissociation, photosensibilisée par le mercure, d'un précurseur choisi contenant de l'oxygène.

7. Procédé selon la revendication 6, dans lequel le précurseur contenant de l'oxygène est du protoxyde d'azote (N_2O), le réactif en phase vapeur est un silane (SiH_4), le procédé est mis en oeuvre dans un réacteur photochimique statique de manière que la SiH_4 soit présent à une pression équivalent à 399,9 Pa (3 mm de mercure) et que le N_2O soit présent à une pression équivalant à 1599,6 Pa (12 mm de mercure), la température à laquelle le procédé est maintenu est de 30 à 200°C, et l'oxyde est du monoxyde de silicium.

8. Procédé selon la revendication 6, dans lequel le précurseur contenant de l'oxygène est du protoxyde d'azote (N_2O), le réactif en phase vapeur est un silane (SiH_4), le procédé est mis en oeuvre dans un réacteur photochimique à écoulement continu, de manière que le SiH_4 possède un débit d'écoulement de gaz de 2 cm^3 normalisés par minute et que le N_2O possède un débit d'ecoulement de gaz de 10 cm^3 normalisés par minute, la température à laquelle le procédé est maintenu est de 30 à 200°C, et l'oxyde est du monoxyde de silicium.

9. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le précurseur contenant de l'oxygène est du protoxyde d'azote (N_2O), le réactif en phase vapeur est un silane (SiH_4), la longueur d'onde prédéterminée est de 175—195 nm (1750 à 1950Å), le SiH_4 possède un débit d'écoulement de gaz de 2 cm^3 normalisés par minute, et le N_2O possède un débit d'écoulement de gaz de 50 cm^3 normalisés par minute, la température à laquelle le procédé est maintenu est de 30 à 200°C, et l'oxyde est du bioxyde de silicium (SiO_2).

10. Procédé selon l'une quelconque des revendications 1—5, dans lequel le précurseur contenant de l'oxygène est de l'oxygène moléculaire (O_2) auquel de l'azote (N_2) est mélangé, ladite longueur d'onde prédéterminée est de 184,9 nm (1849Å), le réactif en phase vapeur est un silane (SiH_4), ladite pression est de 0—662,5 Pa (0 à 5 mm de mercure), le débit d'écoulement gazeux des SiH_4, O_2 et N_2 sont, respectivement, de 1, 20 et 80 cm^3 normalisés par minute, et l'oxyde est du bioxyde de silicium.

11. Procédé selon la revendication 5 ou 6, dans lequel la matière contenant un dope est de la phosphine (PH_3), du diborane (B_2H_6), de l'arsine (AsH_3), de la stibine (SbH_3), du séléniure d'hydrogène (H_2Se), de l'hydrogène sulfuré (H_2S) ou du tellure d'hydrogène (H_2Te).

12. Procédé selon la revendication 6, dans lequel le précurseur contenant de l'oxygène est du protoxyde d'azote (N_2O), le réactif en phase vapeur est un silane (SiH_4), la longueur d'onde prédéterminée est 253,7 nm (2537Å), les débits d'écoulement gazeux des SiH_4 et N_2O

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sont de 2 et 50 cm^3 normalisés par minute, respectivement, la température à laquelle le procédé est maintenu est de 30 à 200°C, et l'oxyde est du bioxyde de silicium.

Patentansprüche

1. Verfahren zum Aufbringen einer Oxidschicht eines vorgegebenen Materials auf die Oberfläche eines ausgewählten Substrates mit den Verfahrensschritten, daß das Substrat einem dampfförmigen Reagens und einer chemisch nicht reaktiven, gasförmigen, sauerstoffhaltigen Ausgangsverbindung in Anwesenheit einer Strahlung vorbestimmter Wellenlänge ausgesetzt wird, die eine Dissoziation der sauerstoffhaltigen Ausgangsverbindung und eine Erzeugung neutraler Sauerstoffatome bewirkt, welche mit dem dampfförmigen Reagens reagieren und die Oxidschicht auf der Oberfläche des Substrates unter ausgewählten Bedingungen für Temperatur, Druck und Durchflußrate bilden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das dampfförmige Reagens Silizium, Germanium, Gallium, Bor, Indium, Aluminium, Titan, Wolfram oder Hafnium enthält.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das dampfförmige Reagens Silan (SiH_4) und das Oxid Siliziumdioxid und/oder Siliziummonoxid ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung Stickstoffoxid (N_2O), Stickstoffdioxid (NO_2) oder molekularer Sauerstoff (O_2) bie vorgewähltem Druck und Durchflübrate ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Oxidschicht in Anwesenheit eines gasförmigen, dotierstoffhaltigen Materiales ausgebildet wird, sodaß Atome des Dotierstoffes in das Oxid eingebaut werden.

6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß Queksilberdampf dem Reagens und der Ausgangsverbindung zugefügt wird, sodaß eine durch Quecksilber photosensibilisierte Dissoziation einer ausgewählten sauerstoffhaltigen Ausgangsverbindung eintritt.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung Stickstoffoxid (N_2O) ist, das dampfförmige Reagens Silan (SiH_4) ist, daß das Verfahren in einem statischen photochemischen Reaktor ausgeführt wird, wobei der Druck des SiH_4 399,9 Pa (3 mm Quecksilbersäule) und derjenige des N_2O 1599,6 Pa (12 mm Quecksilbersäule) beträgt, daß die Temperatur, bei der das Verfahren abläuft, im Bereich zwischen 30 bis 200°C liegt und daß das Oxid Siliziummonoxid ist.

8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung Stickstoffoxid (N_2O) ist, daß das dampfförmige Reagens Silan (SiH_4) ist, daß das Verfahren in einem photochemischen Reaktor mit kontinuierlichem Durchfluß abläuft, wobei das SiH_4 eine Durchflußrate von 2 Standard-Kubikzentimetern pro Minute und das N_2O eine solche von 10 Standard-Kubikzentimetern pro Minute hat, daß die Temperatur, bei der das Verfahren abläuft, im Bereich von 30 bis 200°C liegt, und daß das Oxid Siliziummonoxid ist.

9. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung Stickstoffoxid N_2O ist, daß das dampfförmige Reagens Silan (SiH_4) ist, daß die vorbestimmte Wellenlänge 175 bis 195 nm (1750 bis 1950Å) beträgt, daß die Durchflußrate des SiH_4 2 Standard-Kubikzentimeter pro Minute und diejenige des N_2O 50 Standard-Kubikzentimeter pro Minute beträgt, daß die Temperatur, in welcher das Verfahren abläuft, im Bereich zwischen 30 und 200°C liegt, und daß das Oxid Siliziumoxid (SiO_2) ist.

10. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung molekularer Sauerstoff (O_2) ist, daß Stickstoff (N_2) hinzugemischt wird, daß die vorbestimmte Wellenlänge 184,9 nm (1849Å) ist, daß das dampfförmige Reagens Silan (SiH_4) ist, daß der Druck 0 bis 662,5 Pa (0 bis 5 mm Quecksilbersäule) beträgt, daß die Durchflußraten des SiH_4 bzw. O_2 bzw. N_2 den Wert von 1 bzw. 20 bzw. 80 Standard-Kubikzentimeter pro Minute aufweisen, und daß das Oxid Siliziumdioxid ist.

11. Verfahren nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß das dotierstoffhaltige Material Phosphorwasserstoff (PH_3), Diboran (B_2H_6), Arsenwasserstoff (AsH_3), Antimonwasserstoff (SbH_3), Selenwasserstoff (H_2Se), Schwefelwasserstoff (H_2S) oder Tellurwasserstoff (H_2Te) ist.

12. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die sauerstoffhaltige Ausgangsverbindung Stickstoffoxid (N_2O) ist, daß das dampfförmige Reagens Silan (SiH_4) ist, daß die vorbestimmte Wellenlänge 253,7 nm (2537Å) beträgt, daß die Durchflußate des SiH_4 bzw. des N_2O den Wert von 2 bzw. 50 Standard-Kubikzentimetern pro Minute aufweist, daß die Temperatur, bei der das Verfahren abläuft, im Bereich von 30 bis 200°C eingestellt wird und daß das Oxid Siliziumdioxid ist.

* C L M S *