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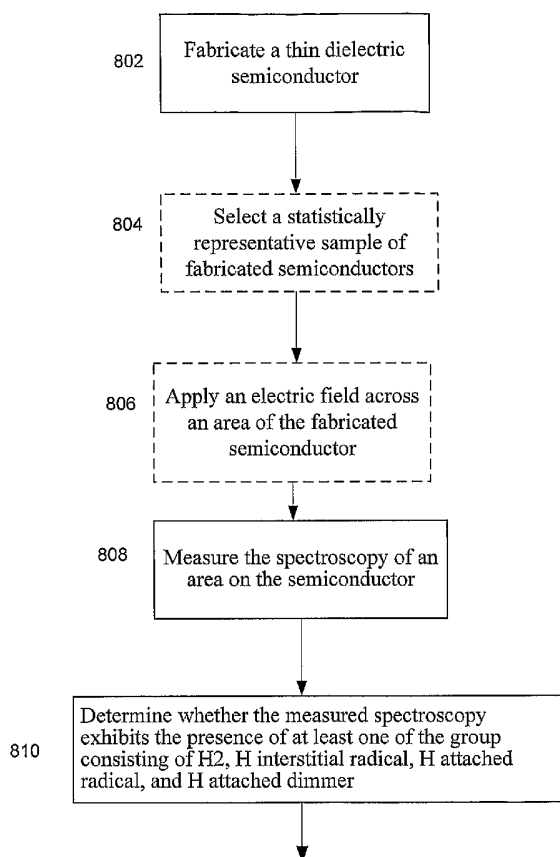
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(54) Title: DETECTION AND REDUCTION OF DIELECTRIC BREAKDOWN IN SEMICONDUCTOR DEVICES



(57) Abstract: Methods for detecting the breakdown potential of a semiconductor device having a thin dielectric layer are disclosed. The method includes measuring a spectroscopy of the thin dielectric layer and determining whether the spectroscopy exhibits the presence of a breakdown precursor (H₂, H interstitial radical, H attached radical, and H attached dimer). Preferably, the method is carried out in the presence of a substantially significant applied electric field across dielectric layer. A semiconductor device tested in accordance with this method is also disclosed. Additionally, methods for reducing dielectric breakdown of a semiconductor device having a thin dielectric layer involving the substitution of a second molecule for H₂ molecules present in the dielectric. This second molecule preferably does not react with Si or O to form an undesired attached state and may be an inert gas having a molecular size approximating that of a Hydrogen atom, such as Helium. A semiconductor device made using this method is also disclosed.

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DETECTION AND REDUCTION OF DIELECTRIC BREAKDOWN
IN SEMICONDUCTOR DEVICES

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims benefit under 35 U.S.C. §119(e) to provisional patent application serial number **60/506,453** filed on September 26, 2003 entitled "Mechanism of Dielectric Breakdown."

BACKGROUND OF THE INVENTION

10 1. Field of the Invention

 The present invention is directed to methods for improving semiconductor devices and, in particular, to methods and apparatuses for the detection and reduction of dielectric breakdown in such devices.

 2. Background Art

15 In general, the gate oxide thickness for the current generation of field-effect transistors (FET) is approximately 50 Angstroms. The next generation of FETs will require thinner oxides in order to achieve desired miniaturization. However, with current technology the electron current that would leak through a thinner gate oxide during transistor usage would be too large to prove useful. In fact, such large leakage currents would likely lead to
20 permanent damage of the oxide layer, potentially damaging the FET in minutes. These leakage currents are thought to be due to dielectric breakdown in the insulating layers. This makes dielectric breakdown a critical issue in the miniaturization of FETs and other semiconductor devices. Yet, little, if anything, is understood about the mechanism responsible for dielectric breakdown in thin dielectric layers in electronic devices.

25 It is known the operating electric field increases as the dielectric thickness decreases. The electric field is the ratio of the applied voltage across the dielectric and its thickness. If the thickness is reduced by a factor of 2, then one could maintain exactly the same electric field by reducing the applied voltage by the same factor of 2. Unfortunately, one cannot scale the gate voltage down proportionally to the thickness because the voltage becomes too small
30 to control the current across the FET between the source and drain. Thus, thinner dielectrics must operate with higher electric fields.

SUMMARY OF THE DISCLOSURE

 The present disclosure uses quantum mechanics and molecular dynamics studies to derive a mechanism for breakdown in thin dielectrics. In particular, the present disclosure

uses the case of silicon dioxide (SiO_2) gate materials in field-effect transistors (FET) to illustrate that the significantly larger electric fields associated with thin dielectrics cause H (“hydrogen interstitial radical”) that can arise from H_2 (“hydrogen dimer”) to react with defects and irregularities that occur inside the thin dielectric (insulator) and at its interface with the semiconductor (“insulator-semiconductor interface”).

Hydrogen dimer (H_2) is a bound complex of two hydrogen atoms and is known to be ubiquitous inside current dielectrics. H_2 was never considered to be the source of dielectric breakdown. However, the present disclosure shows the surprising result that the reaction of H_2 with the defects and irregularities in the semiconductor device causes situations that can lead to increased leakage current and breakdown.

The present disclosure also teaches methods for reducing or eliminating the breakdown problem. In one aspect of the invention, the H_2 is pumped off and replaced with helium (He), for example. In addition, the present disclosure also teaches methods for detecting the potential failure by in situ or ex situ monitoring of spectroscopic and other characteristics of the sites causing breakdown, their precursors, and the presence of the H_2 and He.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 of the drawings is a molecular model showing an H atom in an interstitial location (“H interstitial radical”) in SiO_2 .

Fig. 2 of the drawings is molecular model showing an H atom attached (“attached radical”) to an O atom that is part of the SiO_2 structure.

Fig. 3 of the drawings is a graph comparing the computed energies of an interstitial H in SiO_2 relative to an attached H in SiO_2 as a function of an external electric field.

Fig. 4 of the drawings is a molecular model showing two H atoms attached at neighboring O sites (“attached dimer”) in SiO_2 .

Fig. 5 of the drawings is a graph of two different computed relative energies: 1.) two H interstitial “apart” states minus H_2 , and 2.) the attached dimer state minus H_2 dimer. Both lines are shown as a function of the external electric field.

Fig. 6 of the drawings is a schematic representation of the energy loss to phonons from the acceleration of the electron through attached states.

Fig. 7 of the drawings is a graphical representation of the computed energies for the creation of an attached H state in a zero electric field in the vicinity of a Si dangling bond.

Figs. 8a and 8b of the drawings are a flow diagram of a preferred approach for manufacturing a semiconductor device having a thin dielectric layer and detecting the breakdown potential thereof.

Fig. 9 of the drawings is a flow diagram of a first approach to reducing the dielectric
5 breakdown in a semiconductor device having a thin dielectric layer.

Fig. 10 of the drawings is a flow diagram of a second approach to reducing the dielectric breakdown in a semiconductor device having a thin dielectric layer.

Fig. 11 of the drawings is a flow diagram of a third approach to reducing the dielectric breakdown in a semiconductor device having a thin dielectric layer.

BEST MODES OF CARRYING OUT THE INVENTION

The present disclosure teaches various methods for detecting the breakdown potential of a semiconductor device having a thin dielectric layer and methods for reducing that dielectric breakdown potential. Although the present specification is described in terms of SiO₂ field-effect transistors (FET), those working in the semiconductor processing industry generally understand that SiO₂ reacts much the same way as other semiconductor materials.

The semiconductor industry, as a whole, is generally trying to decrease oxide thicknesses to achieve increased device miniaturization. The existence of H₂ in dielectrics is widely known to be caused by all semiconductor processing methods. However, prior to the present invention, the existence of H₂ in dielectric materials was believed by the industry to be benign.

In semiconductor devices, as the dielectric (oxide) thickness is reduced, the size of the electric field inside the gate increases significantly. As a result of this significantly increased electric field, technologically relevant applied electric fields (about 10 million volts per centimeter or 10 MV/cm) lead to new chemical reactions not experienced previously. Some combination of this increased electric field and these resulting chemical reactions create novel electronic states in the dielectric that strongly increase the current flow of the dielectric and cause breakdown.

First, there is a particular state where a hydrogen atom “attaches” or weakly bonds to an oxygen atom in SiO₂ that can cause electron tunneling and breakdown. Based on quantum mechanical and force-field studies, this attached state was found to be 1.0 eV (electron volts) higher than the previously known interstitial hydrogen state in zero electric field. In an applied electric field, this attached state can become more stable than the interstitial state. In addition, two attached H states nearby can be further stabilized due to their large hybridization (attached dimer state).

Second, there are two different chemical reactions that can create thermally accessible attached H dimer states under an applied electric field: (1) cracking H₂ in an interstitial region; and (2) cracking H₂ near a Silicon dangling bond (Pb center) near the Si-SiO₂ interface, $H_2 + Si \rightarrow Si-H + (\text{attached } H)$. Figure 1 shows the well-characterized H atom in an interstitial location in a SiO₂ lattice. Figure 2 shows a state with the H atom “attached” to an O atom that is 1.0 eV higher in energy. This state leads to an asymmetry in the Si-O bond lengths of the two Si bonded to the O attached to H. The O atom shifts 0.5 Angstroms towards H.

Figure 3 compares the energies of an interstitial H in SiO₂ relative to an attached H in SiO₂ as a function of an external electric field. These results are for a two dimensional SiO₂ slab terminated with H atoms. The field is applied in the upward direction in Figures 1 and 2. Since the dielectric constant of SiO₂ is approximately 4, the internal field is 1/4 the external field value. Thus, for experimental fields from 10-20MV/cm, or 40-80MV/cm applied fields, the attached state is lower in energy than the apart state. Thus, the attached state becomes energetically favorable (more stable) for external fields larger than 40 MV/cm (million volts per centimeter).

In other words, as the foregoing describes, the strong electric field changes the chemistry of hydrogen bonding. The strong electric field makes a new quantum state accessible. The attached state has a large diffuse orbital with large amounts of charge on the nearby O and Si sites. This state will hybridize strongly with any other nearby attached state and lead to states in the SiO₂ bandgap with a large coupling to the metal electrodes generally found on each side of the gate oxide. The hybridization energy has been calculated to be 1.4eV. This hybridized "attached dimer" state is shown in figure 4.

Figure 5 compares the relative energies of the attached dimer state to interstitial H₂ as a function of an external electric field. For sufficiently large electric fields, the attached dimer states becomes favorable. In particular, in the graphed example, the attached dimer state becomes energetically favorable (more stable) for external fields larger than 100 MV/cm. Using the dielectric constant of 4 as before, the experimental field is 25 MV/cm for the creation of the attached dimer.

The computed energies discussed above were calculated for the specific case of SiO₂ in a crystalline form (alpha quartz). In reality, SiO₂, like other dielectrics, is amorphous (irregular or disordered). This leads to strained Si-O bonds. The required electric fields for the creation of attached states will be reduced from the computed values for alpha-quartz for attachment to the strained bonds. Our estimates of the necessary electric fields for attached states are therefore higher (more conservative) than what is actually required.

Electron tunneling will occur between the attached dimers and these electrons can dissipate energy into the gate through phonons arising from the acceleration of the electron in the applied electric field. Figure 6 shows a schematic of energy lost to phonons from acceleration of the electron through attached states.

The approximate observed reversibility of breakdown can be understood from electric field induced chemistry. For thicker dielectrics, the electric field is never large enough to make the attached state accessible and hence there is no breakdown. For thinner dielectrics,

however, the electric field is large enough to make the attached state chemistry accessible and easy electron tunneling can occur. This will over time lead to permanent damage to the dielectric structure due to the release of phonons in the gate by the mechanism shown in Figure 6. If the field is turned off, then the attached states are lost and the system reverts
5 back to its original state less whatever permanent damage occurred. Thus, one can understand the difference between soft and hard breakdown phenomena.

Figure 7 is another computed H₂ cracking pathway. Figure 7 shows that H₂ cracking to passivate a Si dangling bond at the Si-SiO₂ interface along with the creation of an attached H state is energetically favorable even in zero electric field. Such Si dangling bonds are
10 known to occur near the dielectric-semiconductor interface. This shows the formation of attached states occurs even without an electric field near the interface.

Based on this observed chemistry and novel electric field induced states, methods may be derived to detect and reduce this dielectric breakdown mechanism. In one embodiment, the detection of the potential or imminent failure may be performed by in situ or
15 ex situ monitoring of spectroscopic and other characteristics of the sites causing breakdown, their precursors, and the presence of the H₂ and He.

Figs. 8a and 8b of the drawings are a flow diagram of a preferred approach to manufacturing a semiconductor device having a thin dielectric layer and detecting the breakdown potential thereof. In step 802, a semiconductor device, such as a FET, having a
20 thin dielectric is fabricated. This fabrication may be any of the presently known techniques as well as presently unknown techniques that may be devised in the future. In one approach, a statistically representative sample of the semiconductor devices fabricated in a batch in step 802 are selected for testing, step 804. In another approach, all of the fabricated devices may be desired for testing, thus step 804 would be omitted in those instances.

In step 806, a substantially significant electric field may then be applied to a selected area of the thin dielectric layer of each individual semiconductor device selected for testing. In one embodiment, the location of the selected area may be chosen based upon the location of any leakage current in the semiconductor device. A substantially significant electric field is an electric field (measured in MV *cm⁻¹ or million volts per centimeter) that would cause H₂
30 in an SiO₂ layer of a semiconductor device to react with the defects and irregularities in SiO₂. In certain semiconductor devices that have already experienced breakdown damage, it may be possible to detect the breakdown precursors without application of the significant electric field. Consequently, it may be desirable to test the semiconductor devices without applying the electric field.

In step 808, the spectroscopy of the one selected area of the thin dielectric layer is measured under the application of the substantially significant electric field. In step 810, it is then determined whether the measured spectroscopy exhibits -- based on the criteria taught above -- the presence of at least one breakdown precursor, i.e., H₂, H interstitial radical, H attached radical, and H attached dimer.

In step 812, the intensity of the substantially significant electric field optionally applied in step 806 may be increased. In such a case, the spectroscopy of the area may be measured again (step 814) and analyzed to determine whether this spectroscopy exhibits the presence of at least one breakdown precursor from the group consisting of H₂, H interstitial radical, H attached radical, and H attached dimer (step 816). In step 818, the electric field strength may be increased again to increase the potential for breakdown chemical reactions to occur in the thin dielectric layer. If such increased testing is desired, the method returns to step 812. If not, then the method is concluded. Such increased field strength may be desirable where a semiconductor device has not exhibited the potential for breakdown chemical reactions under the lower field strengths or alternatively to conduct accelerated testing of the device.

Measuring the spectroscopy of the selected area of the thin dielectric layer may be performed using various methods. Based on the foregoing equations, detecting and monitoring changes in H₂ such as those due to the creation of attached H states using Raman and infra-red spectroscopy to observe changes with and without electric field stress can be used during device fabrication to determine device quality and also to screen potentially bad devices. Electron-Spin Resonance (ESR) may also be used for ESR active configurations (eg., the attached H state) and x-ray absorption/scattering (XANES and XAFS) can detect local structural changes in the material.

Electron Spin Resonance Spectroscopy (ESR) may be used to detect H radicals; attached H; attached H dimer; and Si E and E'-centers. The Hydrogen radical is ESR active due to its single unpaired electron. (H₂ is not ESR active because its two electrons are paired in a spin singlet.) Thus, the cracking of H₂ into two H radicals can be observed by detecting the appearance and change in the H radical spin resonance intensity.

When the H radical attaches to an O (oxygen) in SiO₂, the unpaired electron remains unpaired, but goes into a different ESR active state. There is a detectable g-factor (resonance energy) difference between H radical and attached H to O. The decrease of one ESR signal along with the associated increase in the other signal can be used to determine the rate of attaching reactions or H separation reactions.

The attached H dimer state is spin singlet and is not ESR active. Thus, monitoring changes in the H interstitial radical, attached H radical ESR signals along with their intensity changes leads to information on the rate of formation of attached H dimer states. Detecting Si dangling bond ESR and its changes can be used to examine the formation of the above H states in the interface region where the strain energy from joining the oxide and semiconductor materials together makes the formation of the above H states more favorable.

Raman and infra-red (IR) spectroscopy may also be used to detect H₂; attached H radical and dimer; and Si-O bond vibrations. Changes in the Raman and IR signals for H₂ vibrational modes allows the observation of the amount of H₂ along with its cracking to form H radical. Attached H radical and dimer will have distinct detectable vibrational frequencies and intensities that can be monitored.

Optical absorption, reflection, and transmission may be used to detect the attached H radical and dimer states within the SiO₂ bandgap (approximately 9 eV). These states can be detected and monitored by optical absorption, reflection, and transmission arising from exciting a bound attached electron into the conduction band.

Finally, X-ray Absorption Near Edge Structure (XANES) and X-ray Absorption Fine Structure (XAFS) may be used to measure small structural changes arising from the formation of the above H attached and radical states. In this case, the O atom that H attaches to changes position by approximately 0.5 Angstroms.

Fig. 9-11 illustrate three potential embodiments for reducing the dielectric breakdown of a semiconductor device having a thin layer dielectric. In general, reducing the dielectric breakdown is accomplished by substituting H₂ molecules in the interstitial sites of the SiO₂ with elements or molecules that do not react with Si or O to form the undesired attached states as described above. For instance, in one embodiment, the H₂ may be reduced – in turn reducing dielectric breakdown – by pumping it off and replacing it with helium (He) or any other relatively inert gas that has molecular size approximating that of the H atom.

Fig. 9 illustrates a first method for reducing dielectric breakdown. Generally, H interstitial radicals can move easily from one SiO₂ interstitial void to another, while H₂ cannot. In step 902, ultraviolet (UV) light may be applied to a selected area of the thin dielectric layer (for example, oxide gate) in order to break the H₂ molecules into H interstitial radicals. In step 904, pressurized Helium gas may then be applied to the selected area to essentially push the H atoms out of the dielectric while the Helium atoms fill the interstitial region.

In a second embodiment illustrated in Fig. 10, a substantially significant electric field, rather than UV light, may be applied to the selected area in order to break the H₂ molecules into H interstitial radicals (step 1002). Once again, pressurized Helium gas may then be applied to the selected area to essentially push the H atoms out of the dielectric while the Helium atoms fill the interstitial region (step 1004). The applied electric field may also be a pulsed electric field. The length of each pulse may then be adjusted such that the attached radical state can be formed while driving the H interstitial radicals out of the oxide with the pressurized He.

In yet another embodiment illustrated in Fig. 11, the selected area may be grown using known techniques for growing semiconductor layers (step 1102). In step 1104, a pressurized Helium gas may then be flowed into the growing chamber in order to displace the H₂ molecules and replace them with He during the growth process.

While various embodiments of the application have been described, it will be apparent to those of ordinary skill in the art that many more embodiments and implementations are possible that are within the scope of this invention. Accordingly, the invention is not to be restricted except in light of the attached claims and their equivalents.

CLAIMS

1. A method of detecting the breakdown potential of a semiconductor device having a thin dielectric layer, the method comprising:

- measuring a spectroscopy of at least one selected area of the thin dielectric layer; and

- determining whether the spectroscopy of the at least one selected area of the thin dielectric layer exhibits the presence of at least one breakdown precursor from the group consisting of H₂, H interstitial radical, H attached radical, and H attached dimer.

2. The method according to Claim 1 further comprising applying a substantially significant applied electric field across the at least one selected area of the thin dielectric layer while measuring the spectroscopy of the at least one selected area of the thin dielectric layer.

3. The method according to Claim 2 further comprising:

- increasing the substantially significant applied electric field across the at least one selected area of the thin dielectric layer by a predetermined amount after measuring the spectroscopy of the at least one selected area of the thin dielectric layer; and

- determining whether the spectroscopy of the at least one selected area of the thin dielectric layer under the influence of the increased applied electric field exhibits the presence of at least one breakdown precursor from the group consisting of H₂, H interstitial radical, H attached radical, and H attached dimer.

4. The method according to Claim 2 further comprising:

- repetitively increasing the substantially significant applied electric field across the at least one selected area of the thin dielectric layer by the predetermined amount after measuring the spectroscopy of the at least one selected area of the thin dielectric layer; and

- for each repetitive increase of the substantially significant applied electric field, determining whether the spectroscopy of the at least one selected area of the thin dielectric layer under the influence of the increased applied electric field exhibits the presence of at least one breakdown precursor from the group consisting of H₂, H interstitial radical, H attached radical, and H attached dimer.

5. The method according to Claim 2 further comprising selecting the at least one selected area of the thin dielectric layer for measurement based upon the location of a leakage current in the semiconductor device.

6. The method according to Claim 2 wherein measuring the spectroscopy includes the step of using Electron Spin Resonance Spectroscopy to measure the physical characteristics

caused by the at least one selected from the group consisting primarily of Hydrogen ESR, Attached H ESR, Attached H dimer ESR and Si E and E'-center ESR.

7. The method of Claim 6 wherein measuring the spectroscopy further includes the step of using infra-red spectroscopy to measure the physical characteristics caused by the at least one selected from the group consisting primarily of H₂, attached H radical and dimer, and Si-O bond vibrations.

8. The method according to Claim 7 wherein the infra-red spectroscopy is performed with a Raman Spectroscope.

9. The method according to Claim 2 wherein measuring the spectroscopy includes the step of using Glancing Incidence X-Ray Reflection/Refraction (GIXR) to measure the physical characteristics caused by small spatial density changes in the interface (Metal/SiO₂) region caused by the formation of the above H attached and radical states.

10. The method according to Claim 2 wherein measuring the spectroscopy includes the step of using optical absorption, reflection, and transmission to measure the physical characteristics caused by the group consisting of attached H radical and dimer states.

11. The method according to Claim 2 wherein measuring the spectroscopy includes the step of using X-ray Absorption Near Edge Structure (XANES) to measure small structural changes arising from the formation of the above H attached and radical states.

12. The method according to Claim 2 wherein measuring the spectroscopy includes the step of using X-ray Absorption Fine Structure (XAFS) to measure small structural changes arising from the formation of the above H attached and radical states.

13. A semiconductor device tested in accordance with the method of Claim 1.

14. A semiconductor device tested in accordance with the method of Claim 2.

15. A semiconductor device manufactured as part of a batch wherein a statistically representative sample from the batch is tested in accordance with the method of Claim 1.

16. A semiconductor device manufactured as part of a batch wherein a statistically representative sample from the batch is tested in accordance with the method of Claim 2.

17. A method for reducing dielectric breakdown of a semiconductor device having a thin dielectric layer, the method comprising:

substituting an H₂ molecule in at least one selected area of the thin dielectric area with a second molecule.

18. The method of Claim 17 wherein the second molecule does not react with Si or O to form an undesired attached state.

19. The method of Claim 17 wherein the second molecule is an inert gas having a molecular size approximating that of a Hydrogen atom.
20. The method of Claim 17 wherein the second molecule is helium.
21. The method of Claim 17 wherein substituting includes growing the at least one selected
5 are in the presence of pressurized flowing He.
22. The method of Claim 17 wherein substituting includes:
 applying ultra-violet light to the at least one selected area; and
 applying a pressurized He gas to the at least one selected area.
23. The method of Claim 17 wherein substituting includes:
10 applying a substantially significant electric field to the at least one selected area; and
 applying a pressurized He gas to the at least one selected area.
24. The method of Claim 23 wherein the substantially significant electric field is a pulsed electric field.
25. A semiconductor device made using the method of Claim 17.
- 15 26. A semiconductor device made using the method of Claim 18.

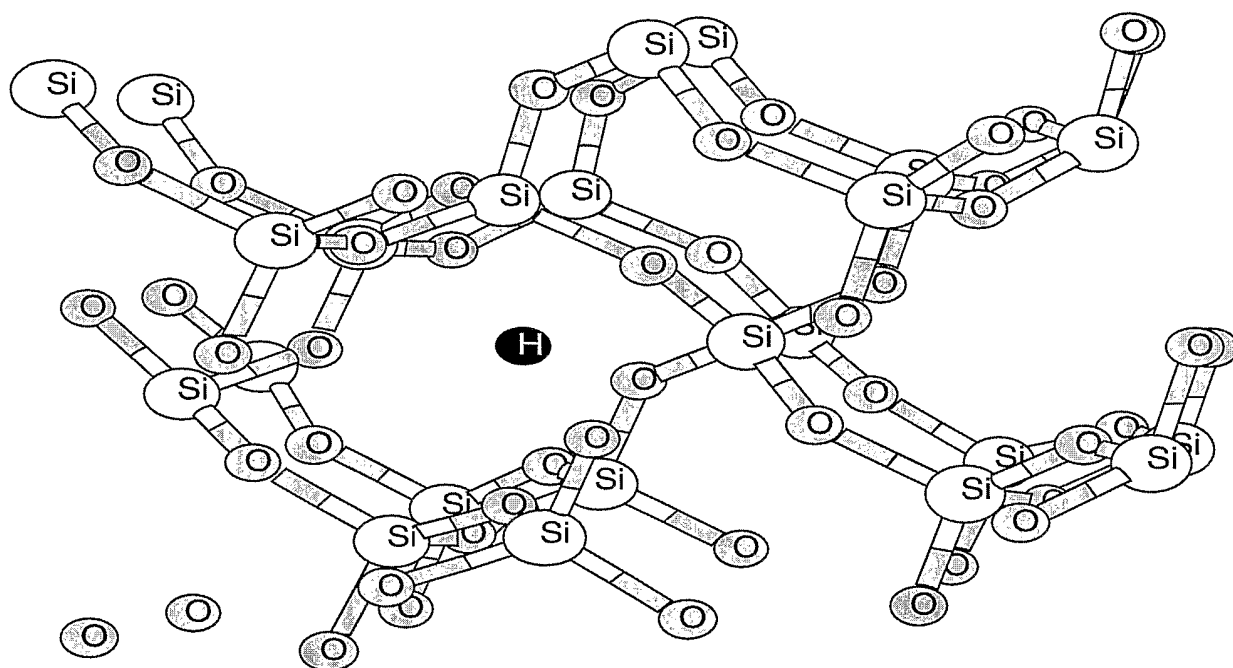


Fig. 1

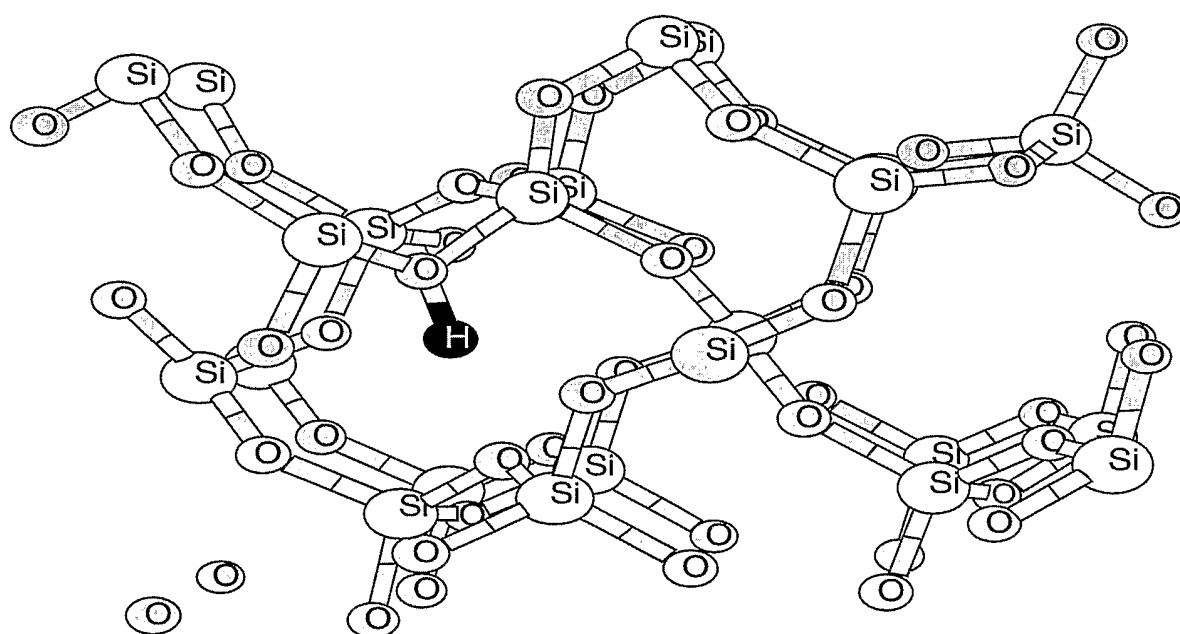


Fig. 2

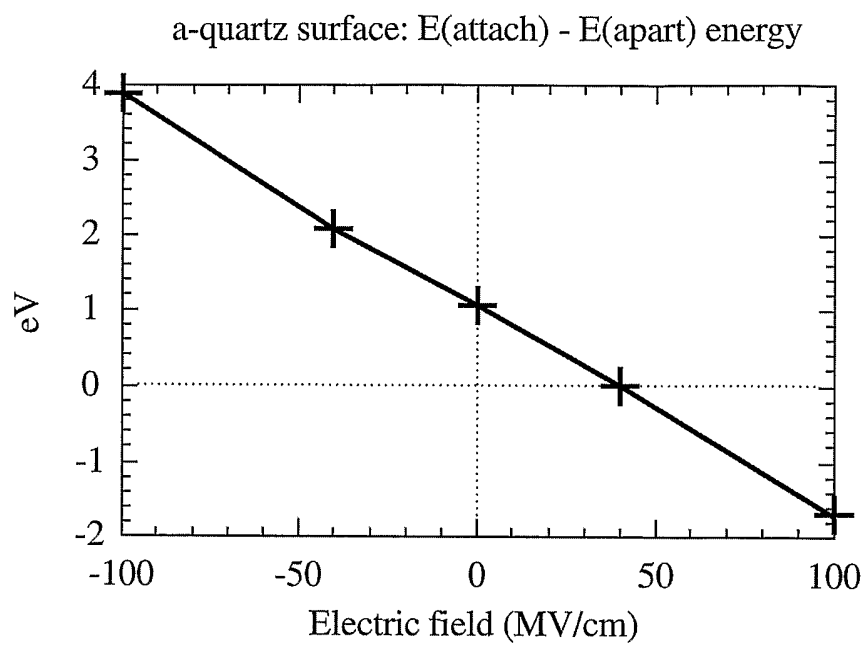


Fig. 3

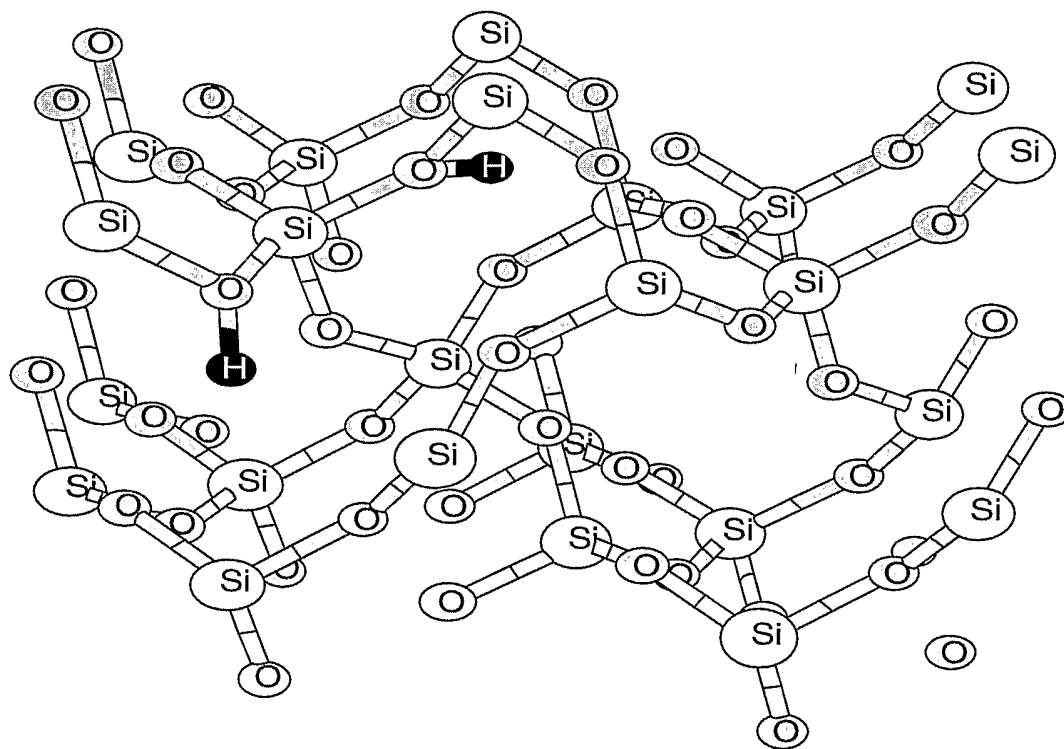


Fig. 4

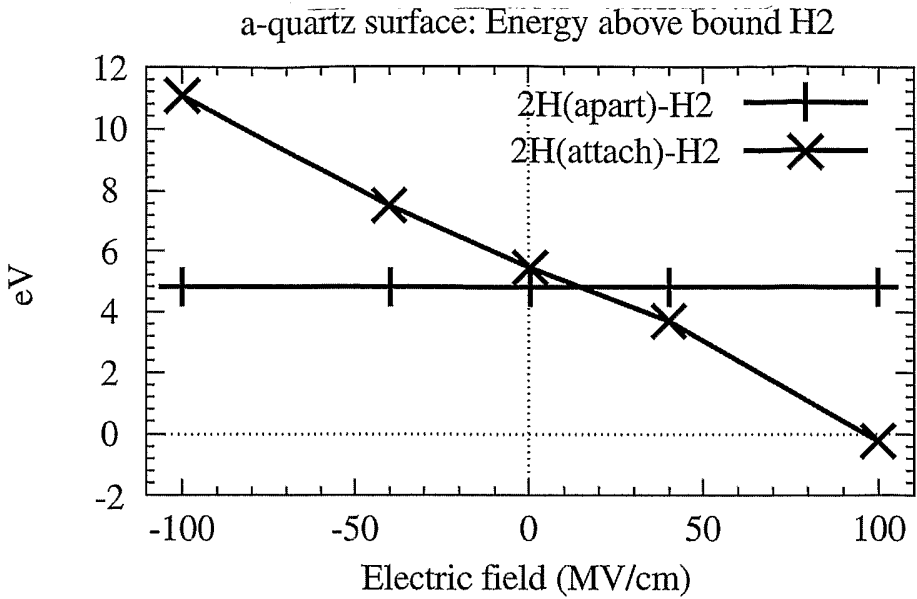


Fig. 5

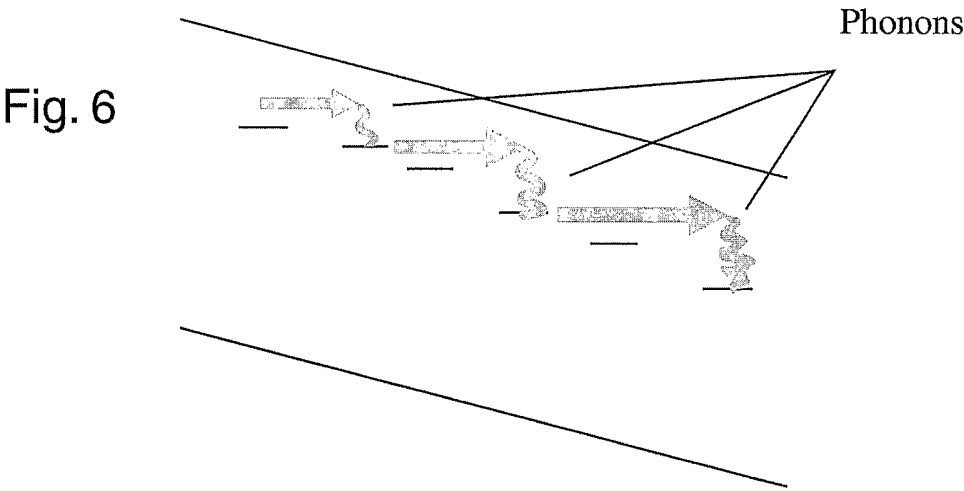


Fig. 6

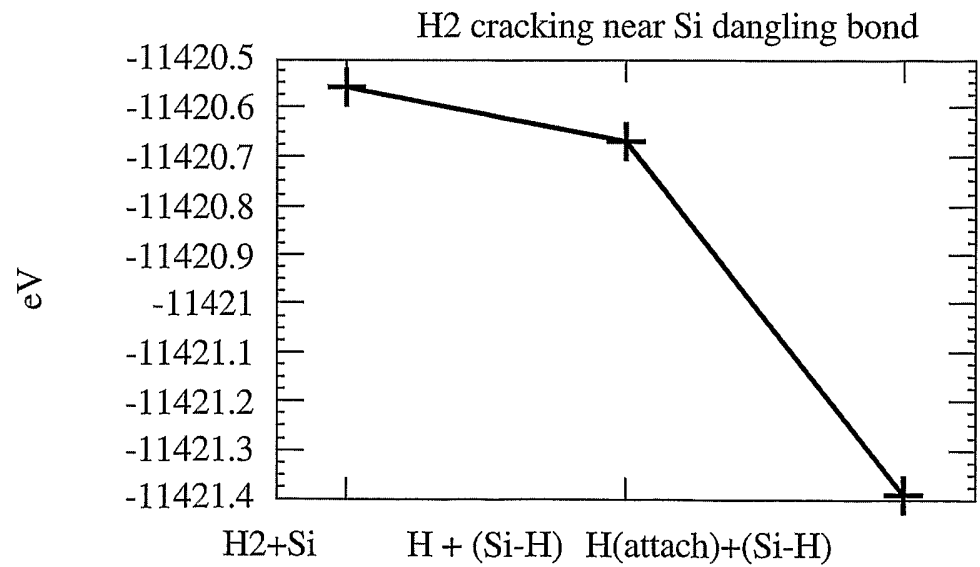


Fig. 7

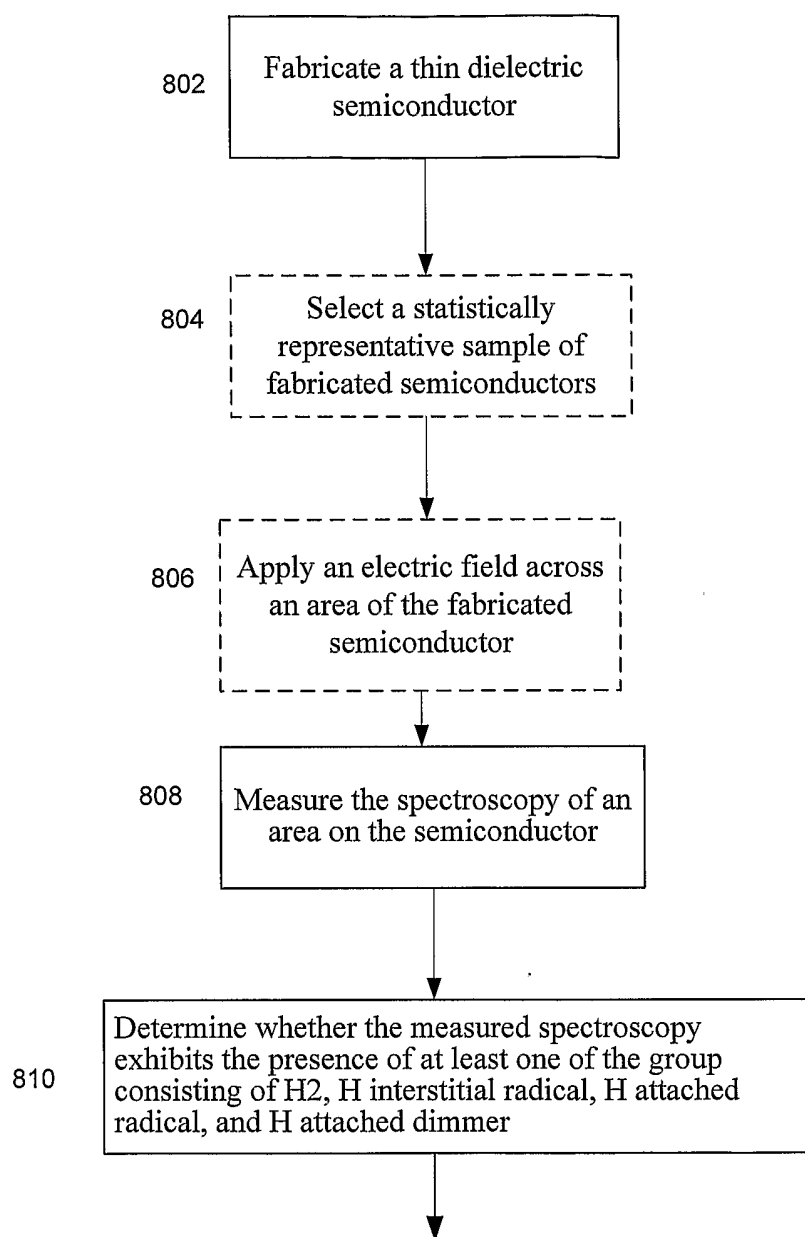


FIG. 8a

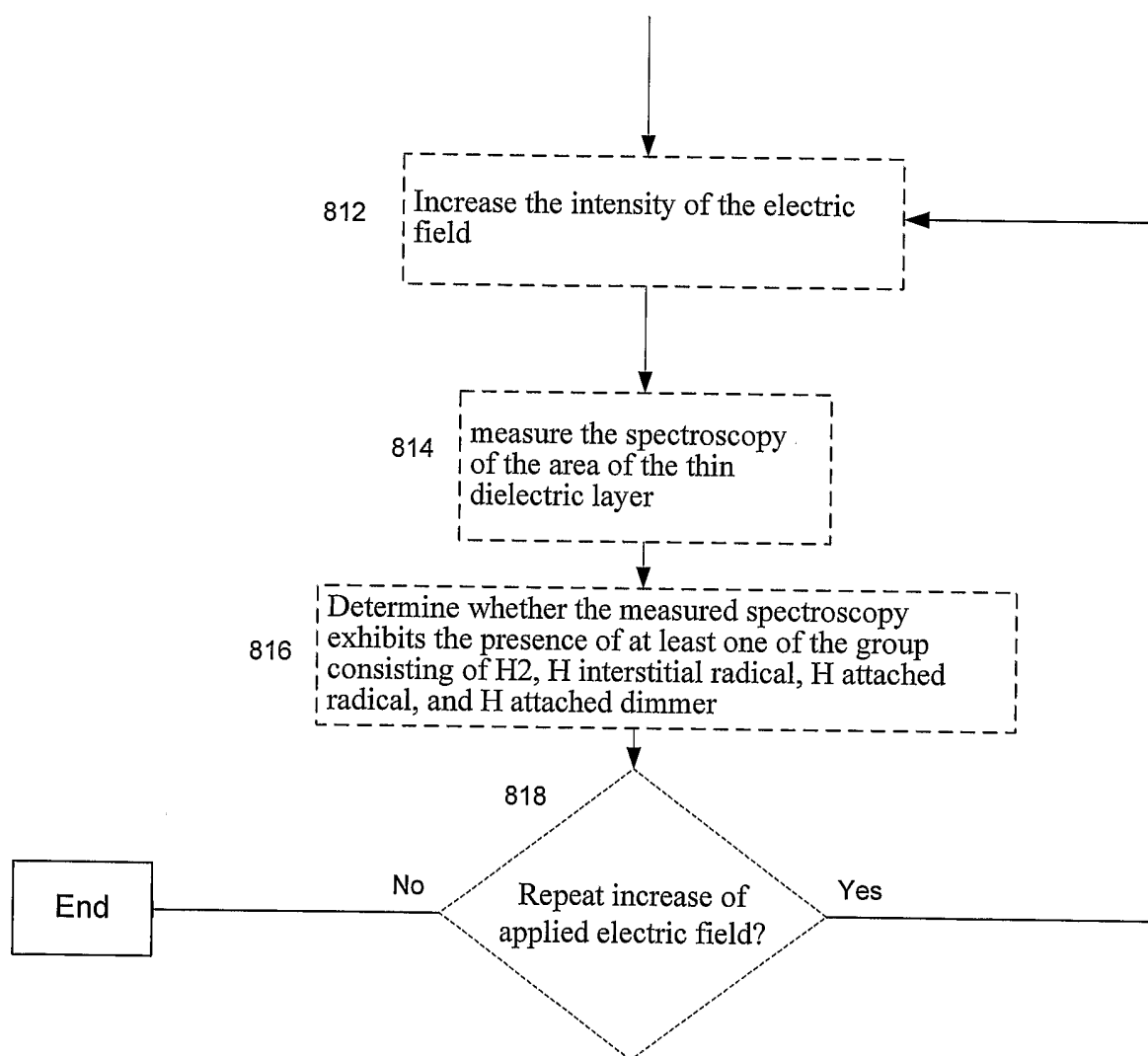


FIG. 8b

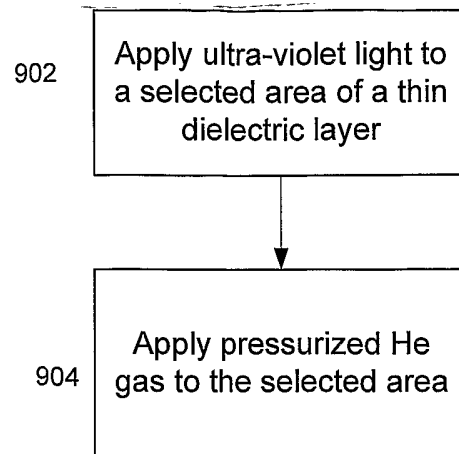


FIG. 9

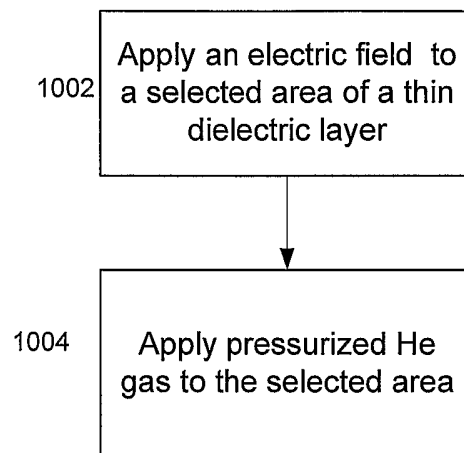


FIG. 10

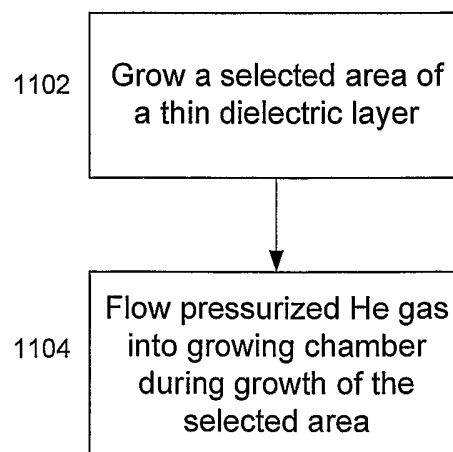


FIG. 11