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Dielectric Films for Ge Planar Devices

Abstract: A series of passivating and masking films was developed and evaluated for use in a Ge planar transistor technology. In the search for satisfactory films, silicon dioxide, aluminum oxide, silicon nitride and multilayer combinations of these films, as well as some doped and mixed-composition films, were studied. The films, formed by pyrolytic deposition or by sputtering, were evaluated and compared with respect to the following properties: etch rate; dopant masking; mechanical stress; oxygen, hydrogen and water permeability; stability with respect to elevated temperature electrical-bias stressing; and Ge-insulator interface electrical condition.

The most important results of our experiments are the following: Silicon nitride appears to be the only satisfactory mask for Ga diffusions, although silicon dioxide is adequate for As, P and Sb diffusion masking. The dielectric properties of pyrolytically deposited SiO_2 can be made to approach those of thermal SiO_2 by high temperature densification. The surface electrical properties of the Ge-SiO_2 interface are more stable to thermal annealing than is any other Ge-insulator combination. However, aluminum oxide has been shown to be much less permeable to oxygen, hydrogen and water vapor than is SiO_2. Since the Ge-insulator interface electrical properties are sensitive to these ambient gases, a satisfactory passivating film structure for Ge consists of an underlayer of SiO_2 and an overlayer of Al_2O_3, silicon nitride or other relatively impermeable film.

Introduction

Although Ge was the first semiconductor transistor material, it has been largely superseded by Si because the latter forms a high quality, easily grown oxide film that makes planar technology possible. Germanium oxide has the serious disadvantage of being somewhat water soluble, which renders it unusable in the many aqueous etching steps necessary for planar transistor fabrication and inadequate for passivation in moisture-bearing atmospheres. Several attempts have been made to produce the tetragonal crystalline modification of GeO_2, which is water insoluble.[1,2] The relative difficulty in producing the tetragonal form of the oxide, and the supposition that the resulting polycrystalline film probably would not be a good diffusion mask or passivator because of grain boundary diffusion, have led to a search for more promising passivating films.

The use[3] of pyrolytic SiO_2 films made possible the successful fabrication of high-speed Ge integrated circuits.[4] Since the SiO_2 films were necessarily deposited at relatively low temperatures (less than 500°C), it was soon realized that the SiO_2 film quality was not equal to that of thermal SiO_2 grown on Si unless a high-temperature densification step had been used after film deposition. Our general approach has been to use other films, primarily Al_2O_3, silicon nitride* and multilayer combinations with SiO_2, deposited at relatively low temperatures by severa different processes. The use of these films solved the major passivating and masking problems in Ge planar technology: (1) diffusion masking against p-type dopants at high temperatures; (2) passivation against O_2 and H_2 diffusion during processing steps; and (3) impermeability to H_2O in accelerated life testing. Also, silicon nitride and Al_2O_3 produced at high temperatures were known[5,6] to be effective sodium ion barriers. In addition to maintaining the desirable film properties of uniformity, etchability and good dielectric characteristics, we tried to understand and control the mechanical stress in the films. Since Ge is more reactive than Si, it was also necessary to avoid film deposition reactants such as ammonia and oxygen, which attack the Ge surface.

In the following sections the preparation and properties of the films and the various techniques that were used to evaluate the films are discussed. Included are dopant diffusion masking, mechanical stress, surface electrical properties, gas permeability during processing, temperature-bias stability and the effects of temperature and humidity. No specific device results are reported here. However, the films that were found to have superior properties have been tried in actual devices and all have yielded good results.

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* The silicon-to-nitrogen ratio in these films is 0.5 rather than the stoichometric value 0.75.

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Preparation and physical properties

Most of the films used in this investigation were formed by chemical vapor deposition.[7] The films studied are listed in Table 1 with the deposition temperature and other properties. The notation for film identification is based on the deposition ambience, which is a major factor determining the electrical interface properties. An important parameter affecting the quality of all the films was the cleanliness of the substrate surface. The chemically polished samples[8,9] were rinsed in HF just before being loaded into the furnace in which deposition took place. Further process details for most of the films are given in the references.

The aluminosilicate films were formed in a nitrogen carrier gas atmosphere in a pyrolytic system, similar to that described by Aboaf,[10] in which provision was made for the introduction of both tetraethylorthosilicate (TEOS) and aluminum isopropoxide. Eversteijn[11] has reported on the deposition and properties of aluminosilicate films in the presence of oxygen at low temperatures. While SiO_2 films cannot be deposited at 420°C in a pure nitrogen atmosphere (see Fig. 1), the thermal decomposition of mixed aluminum isopropoxide and TEOS vapors can produce films of at least 70 wt% SiO_2 in the absence of oxygen (Fig. 2). The film composition becomes independent of the TEOS concentration when the flow through that reservoir exceeds 1 liter/min (at 1.7 liters/min through the aluminum isopropoxide reservoir). The deposition rate, however, continues to increase with increasing TEOS concentration. These properties can be understood if one assumes that the TEOS reacts preferentially with the aluminum isopropoxide and forms a complex compound; this compound would be close to $[Si(OR')_4\,2Al(OR)_3]_n$ (R′ = ethyl and R = isopropyl). The increased formation of this compound with increased TEOS concentration would result in a higher deposition rate for the aluminosilicate film, as is found experimentally.

- *Water permeability*

Moisture is generally regarded as having undesirable effects on semiconductor devices. Marked increases have been noted in the dielectric constant and the dissipation factor of water susceptible films, and adhesion failure resulting from water attack on the Ge-insulator interface has been observed.[12] However, we found no significant effect due to moisture on the fixed charge and surface state densities or in the stability of these parameters under temperature-bias stressing in the films we are describing.

Sensitivity to moisture was evaluated by exposing the films to an atmosphere of 85% relative humidity at 85°C (referred to as T & H stressing) and monitoring the water content through infrared absorption measurements in the 3-μm region[13] with a Beckman IR-10 spectrometer. Samples for T & H stressing were prepared by depositing 5000 to 6000 Å of the appropriate film on 32-mil-thick

Table 1 Preparation conditions and properties of insulating films.

	Preparation conditions				*Properties*		
Film	*Reference*	*Reactant*	*Temperature (°C)*	*Deposition rate (Å/min)*	*Etch rate (Å/sec)*	*Dielectric constant*[h]	*Dissipation factor*[h]
$SiO_2(H_2)$	3	TEOS[a] in forming gas carrier	730	160	125[b], 23[c]	4.2	0.001
$SiO_2(H_2$ dens)	3	Same as $SiO_2(H_2)$; densified in forming gas at 800°C for 18 min			5[c]	3.8	0.0005
$SiO_2(O_2)$	12	TEOS in O_2	450	100	160[b], 26[c]	4.9	0.0015
$P:SiO_2(O_2)$	This paper	TEOS and TEP[d] in O_2	450	≈100		5.8 (for P:Si ≈ 0.15)	
Sputtered Al_2O_3	35	RF-sputtered from 99.5%-Al_2O_3 cathode at 15 W/in.^{2}	≈400	100	18[b]		
$Al_2O_3(N_2)$[e]	10	$Al(OR)_3$[f] in N_2	420	70	33[b], 14[g]	7.7	0.0025
$Al_2O_3(O_2)$	10	$Al(OR)_3$ in O_2	420	70	17[g]	7.7	0.007
Aluminosilicate	This paper	$Al(OR)_3$ and TEOS in N_2	420	100 to 300	33[g]	5 to 6.5	0.005 to 0.007 (for 30 to 80% Al_2O_3)
Silicon nitride (H_2)	17	NH_3 and $SiBr_4$ in forming gas	800	300	1.3[g]	7.5 to 8.5	0.002
Silicon nitride (N_2)	17	NH_3 and $SiBr_4$ in N_2	700	150	2.5[g]	7.5 to 8.5	0.002

[a] Tetraethylorthosilicate.

[b] Buffered HF: 100 mliters 40% NH_4F solution and 13.6 mliters HF.

[c] P-etch: 15 mliters HF, 10 mliters HNO_3 and 300 mliters H_2O.

[d] Triethylphosphate.

[e] Electron microprobe analysis indicated that the ratio of the Al content of the film to that of Al_2O_3 is 1.00, and the ratio of the O content of the film to that of Al_2O_3 is 0.92.

[f] R = isopropyl.

[g] Buffered HF: 113 g NH_4F, 22.7 mliters HF and 166 mliters H_2O.

[h] Measured at a frequency of 10 kHz.

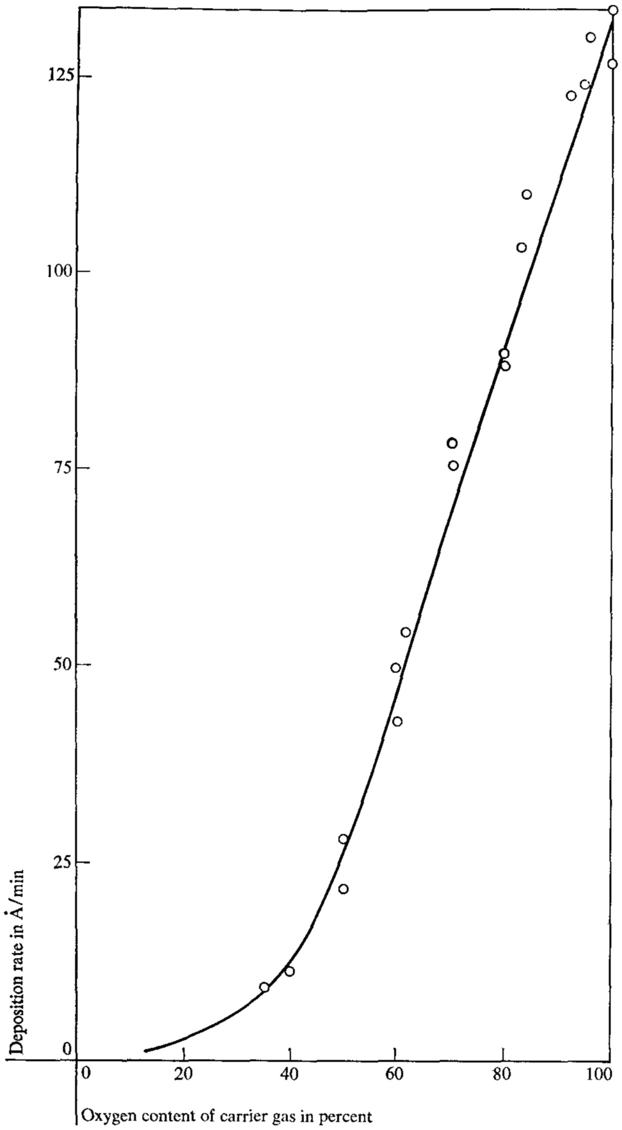

Figure 1 Deposition rate of SiO_2 films at 420°C as a function of the volume percentage of O_2 in the carrier gas.

high-resistivity silicon.* (Only 3000 Å of silicon nitride were used because the high intrinsic stress in this material led to cracking of thicker films.) In these samples 0.4 wt% H_2O could be detected by the OH^- absorption at 3650 cm^{-1}. Retention of more than about 1 wt% H_2O by a film is an indication that the material is excessively permeable.

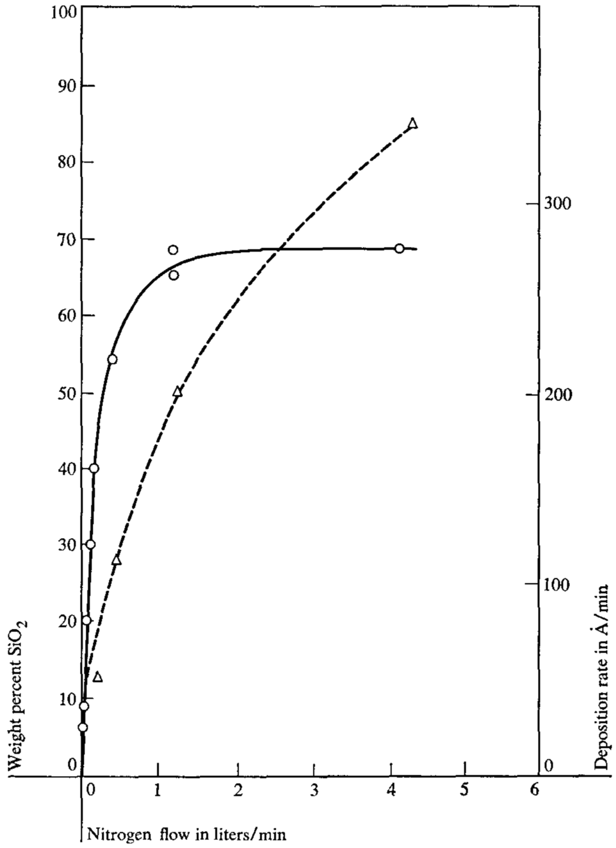

Figure 2 Composition (solid curve) and deposition rate (dashed curve) of aluminosilicate films at 420°C as a function of the N_2 flow through tetraethylorthosilicate (TEOS); the flow through the Al_2O_3 reservoir was 1.7 liters/min.

Table 2 Water content of insulating films after temperature and humidity stressing.

Film	*Initial water content*[a]	*T&H stressing*[b] *(days)*	*Final water content*[a]
$SiO_2(H_2)$	0.013 (0.013)	21	0.05 (0.06)
$SiO_2(H_2$ dens$)$	0.004 (0.008)	21	0.016 (0.021)
$SiO_2(O_2)$	0.04 (0.013)	24	0.076 (0.095)
$P{:}SiO_2(O_2)$	0.022	24	0.086
$Al_2O_3(N_2)$	0.008	59	0.013
Al_2O_3 (sputtered at 400°C)	<0.0004[c]	29	<0.0004[c]
Silicon nitride (N_2)	<0.004	60	<0.004

[a] The water content is reported as the optical density per micrometer at 3650 cm^{-1} (hydrogen-bonded OH^- absorption in SiO_2) and is approximately equal to the weight-fraction of water in SiO_2. For cases in which a band indicating additional adsorbed H_2O could be resolved at 3400 cm^{-1}, the optical density per micrometer at that wave number is given in parentheses.

[b] Although many samples were stressed for long periods, no change in water content was noted after the first few days.

[c] Measurement made by R. Esch using a Perkin Elmer 521 Spectrometer.

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* Silicon, rather than Ge, wafers were used as substrates because, under T&H stressing, the underneath side of a Ge wafer readily forms an oxide which picks up enough water to completely mask the water absorption of the film. Comparison of the initial spectra of films deposited on Ge with the spectra of films deposited on Si shows that the SiO absorption band and the infrared absorption due to the initial water content are essentially the same for both substrates, and thus supports our assumption that film properties are not seriously altered by the choice of a silicon substrate.

Table 3 Water pickup of SiO_2 (O_2) films protected by passivating films.

Passivating film	*Thickness (Å)*	*Initial water content*[a]	*T&H stressing (days)*	*Final water content*[a]
$Al_2O_3(N_2)$	1500	0.030 (0.007)	26	0.029 (0.010)
Sputtered Al_2O_3	1500	0.02 (<0.004)	33	0.014 (<0.004)
Silicon nitride (N_2)	1000	0.006	46	0.006

[a] The water content is reported as the optical density per micrometer at 3650 cm^{-1} (hydrogen-bonded OH^- absorption in SiO_2) and is approximately equal to the weight-fraction of water in SiO_2. For cases in which a band indicating additional adsorbed H_2O could be resolved at 3400 cm^{-1}, the optical density per micrometer at that wave number is given in parentheses.

The water content of the films before and after T & H stressing is shown in Table 2. Among the SiO_2 films, only the densified material had reasonably low initial water content. All the SiO_2 layers showed significant water pickup during T & H stressing, with the undensified SiO_2 being extremely permeable. The silicon nitride and the sputtered Al_2O_3 layers showed essentially no initial water content and excellent resistance to T & H stressing. The pyrolytic Al_2O_3, while having more water initially and greater susceptibility to T & H stressing than the sputtered Al_2O_3, is far superior to SiO_2 deposited at a comparable temperature.

A direct measure of passivating ability was obtained by measuring the effects of T & H stressing on a sample consisting of SiO_2 (O_2) covered by the film to be evaluated.[14] Low moisture pickup by the highly water susceptible SiO_2 (O_2) is an indication that the covering film is an effective barrier to water. Table 3 lists the results of using this structure to evaluate the water permeability of 1000-Å silicon nitride (N_2), sputtered Al_2O_3 and pyrolytic Al_2O_3 (N_2), and shows that these films are indeed effective passivators.

- *Diffusion masking*

In both the silicon and germanium technologies, SiO_2 films (thermal oxide or vapor-deposited oxide at low or high temperature) are not effective as diffusion masks against gallium and indium.[15] Since both of these dopants are useful in Ge circuit fabrication, the effectiveness of other deposited films as diffusion masks against Ga and In was evaluated. Suitable films, in addition to being effective masks, must not in any way damage or permanently perturb the germanium surface. The films should be etchable and the etchant used must not attack the germanium surface.

The diffusion process typically is carried out at 10^{-6} Torr and 800°C for periods of 3h for In and up to 16h for Ga. For the latter, a two-zone furnace with the source at 750°C is used to achieve a Ga surface concentration of 5×10^{19} atoms/cm^3. With indium the source is kept at the same temperature as the sample and the process yields a surface dopant concentration of 4×10^{18} atoms/cm^3.

To evaluate the effectiveness of masking films, 2-mil-wide lines were etched in the layers deposited on germanium and diffusions were made for various lengths of time. The films were then removed by suitable etchants and thermoelectric probe and penetration-depth tests were used to check the conductivity type of the surface and the extent of penetration of the diffusant into the substrate. The results are summarized in Table 4.

Amorphous aluminum oxide films[10] act as diffusion masks for 1h against indium and gallium and can still be removed from the surface with HF after the diffusion. The films do not mask gallium for 3h of diffusion. Heat treatment at 800°C for these times causes the films to crystallize, etching by HF becomes too slow (although hot phosphoric acid is still usable) and diffusion probably occurs along grain boundaries. After a long treatment at 800°C, silicon and germanium surfaces under Al_2O_3 (which also becomes crystalline) exhibit signs of attack in the form of surface etch pits (Fig. 3).

Aluminosilicate films were also tested as diffusion masks. The penetration depth for gallium after a 3-h diffusion through aluminosilicate films of various com-

Table 4 Masking properties of dielectric films against Ga and In diffusion into Ge.

Film	*Thickness (Å)*	*Effective masking time at 800°C (h)*	*Comment*
SiO_2 (H_2)	≈2000	≪1	
Al_2O_3 (N_2)	≈2000	≈1	Films crystallize
Aluminosilicate	≈2000	3 to 16	Films are 70 to 90 wt% Al_2O_3
Silicon nitride (H_2)	300 to 1000	≥16	Thick films plastically deform Ge

Figure 3 Germanium surface (20,000×) after removal of the heat-treated (16h in vacuum at 800°C) Al_2O_3 film.

positions, deposited at 420°C in nitrogen, is shown in Fig. 4. Aluminosilicate films containing from 70 to 90% Al_2O_3 can be used as diffusion masks for gallium. For indium this range is extended to 97% Al_2O_3. These films remain amorphous (as evidenced by x-ray diffraction) and they are easily etchable in HF. For the longer 16-h diffusion no mixture in the binary Al_2O_3-SiO_2 system masked gallium; the aluminosilicate films, while still etchable in buffered HF after the long diffusion, were partially, if not completely, crystallized.

Silicon nitride films obtained by the reaction of silane and ammonia have been evaluated as masks for gallium.[16] We have used silicon nitride films deposited at or below 800°C by the reaction of $SiBr_4$ and ammonia.[17] These films mask very well but, like films obtained by the silane process, they are highly stressed. The subcollector diffusion used in germanium integrated-circuit fabrication is accomplished satisfactorily (i.e., plastic deformation of the substrate due to high stress in the film is avoided) only when a film about 300 Å thick is used (see next section). After the long diffusion this film is still readily etchable in concentrated HF (the nitride film deposited by the silane process is not) and the etching does not damage the germanium surface.

- *Mechanical stress*

One of the problems in depositing thin films on various substrate materials is that of stress. The most serious aspect of the problem occurs when stress in the film exceeds the strength of the film. Amorphous glass films usually fail (i.e., crack) in tension; therefore it is preferable to have the films under compression.

In addition to causing film failure in microelectronic applications, stress will cause elastic bending and, ultimately, plastic deformation of the substrate. Both elastic and plastic deformation can interfere with device processing, particularly in contact photolithography steps (if gross enough), and may also affect the electrical properties of devices.[18] Usually, plastic deformation, which is revealed by the warping of the substrate and by a pattern of fine geometric slip lines crisscrossing the substrate, occurs during high temperature processing because of the decrease in yield strength of both Ge and Si with increasing temperature.[19–21] Since the yield stress of Ge is smaller than that of Si,[20,22] it is even more important in Ge technology to choose film composition, thickness, method of deposition and processing temperatures so that plastic deformation can be avoided.

Hoffman[23] has reviewed extensively the topic of stresses in films as well as the methods for measuring these stresses. The total stress in a film has two components, the thermal stress and the intrinsic stress. Little is known regarding the intrinsic, or residual, component; it appears to be related to the structure of the film. While Hoffman,[23] and more recently Klokholm and Berry,[24] have developed theories to explain the residual stress in metals, no theoretical understanding has yet evolved in the case of thin film dielectrics, especially amorphous ones.

The total stress in films of interest here, as measured at room temperature on germanium substrates by the interference fringe method,[23] is given in Table 5. The salient features of the stress properties of each material are as follows.

SiO_2

Jaccodine and Schlegel[25] and Whelan et al.[26] have found that the source of the compressive stress in thermally grown SiO_2 films on silicon is the difference in the thermal expansion coefficients of the silicon and the film. In the case of SiO_2 (H_2) films deposited on silicon and germanium, the stress cannot be explained solely by the thermal mismatch of film and substrate[27]; it is necessary to postulate an intrinsic tensile stress of $+2.1 \times 10^9$ dyn/cm^2 to explain the observed values of stress. On cooling to room temperature, the thermal mismatch becomes the dominant factor and a compressive stress, reduced in magnitude by the intrinsic tensile stress, is observed. For the conditions of deposition (up to 735°C) and for the thickness of the oxides used in germanium devices (200 Å), the

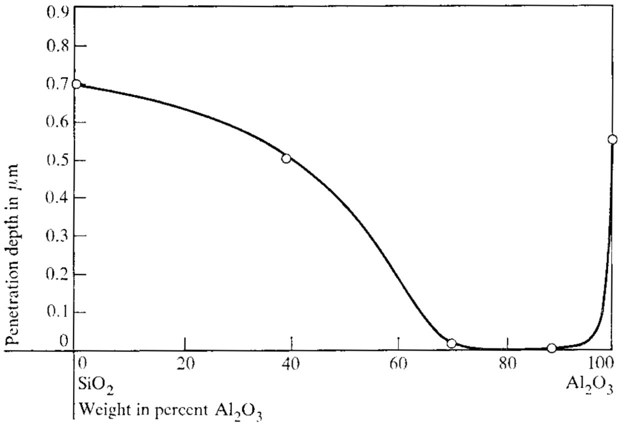

Figure 4 Diffusion of gallium through aluminosilicate films: penetration depth as a function of composition for a 3-h diffusion.

Table 5 Measured stress at room temperature in films deposited on Ge.

Film	Stress[a] ($10^9 dyn/cm^2$)
$SiO_2 (O_2)$	−0.5
$SiO_2 (H_2)$	−1.7
$Al_2O_3 (N_2)$	+4
Sputtered Al_2O_3	−1.2
Silicon nitride (H_2)	+6

[a] A negative value indicates a compressive stress and a positive value, a tensile stress.

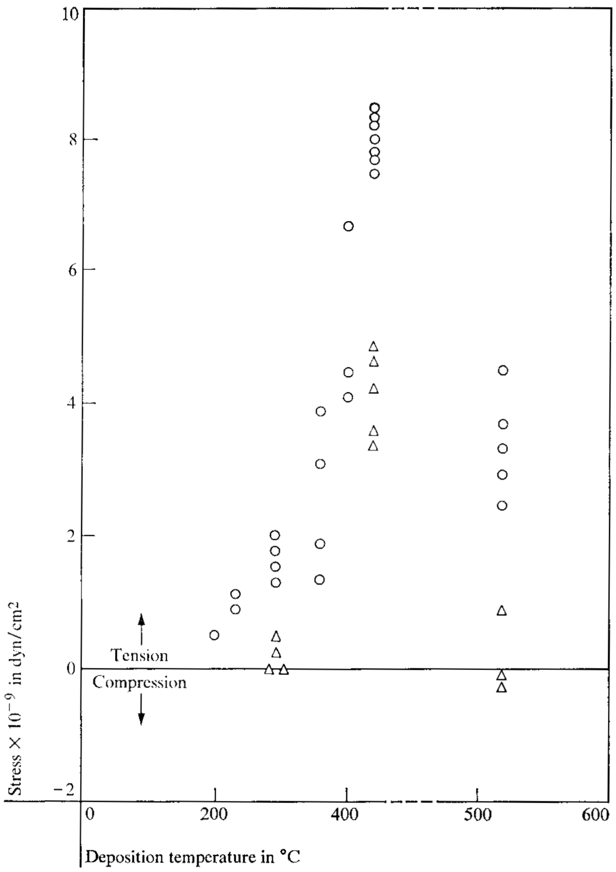

Figure 5 Stresses in Al_2O_3 (N_2) films at room temperature as a function of the deposition temperature. Circles represent data for films on a Si substrate; crosses, a Ge substrate.

substrate (8 to 12 mils) was not plastically deformed by the intrinsic tensile stress. However, if depositions are made at higher temperatures and thicker oxides are used, the germanium substrate may deform plastically and warp.

The stress in SiO_2 (H_2) films deposited on fused quartz discs (an intrinsic stress because there is no mismatch between the film and the substrate) has been measured as $+2.2 \times 10^9$ dyn/cm^2. Comparison with the value cited in the preceding paragraph indicates that the intrinsic stress of SiO_2 (H_2) films is not dependent on whether the film is deposited on silicon, germanium or fused quartz.

Al_2O_3 (N_2)

Pyrolytic Al_2O_3 (N_2) films[28] deposited on germanium are in tension. The stress measured at room temperature in Al_2O_3 films deposited on silicon and germanium at various temperatures is shown in Fig. 5. At about 400°C there is a large increase in the magnitude of the stress relative to the value measured at room temperature. This could indicate a phase transformation; however, all films deposited by this method are amorphous. Films deposited below 400°C are soft* and the stress may have been relieved during growth. The stress at room temperature in Al_2O_3 (N_2) films is independent of the thickness of the film for values between 300 and 7000 Å.

It is not possible at present to calculate the thermal stress between the amorphous film and the substrate because the coefficient of thermal expansion and the modulus of elasticity of amorphous Al_2O_3 are not known. If an amorphous pyrolytic Al_2O_3 (N_2) film deposited on Si at 420°C is heat treated at 800°C or higher, the film crystallizes and develops an increased stress at room temperature, as shown in Table 6. This stress can be accounted for[28] as the thermal stress due to the difference in coefficients of expansion of the substrate and crystalline Al_2O_3. The lower stress in amorphous films results from a different coefficient of expansion or the presence of an intrinsic stress, and possibly from both of these effects.

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* These films can be scratched by stainless steel tweezer tips. Water was detected in these films by infrared absorption measurements; no carbon was detected by electron microprobe analysis.

Table 6 Measured stress at room temperature in Al_2O_3 films deposited on Si.

Film	*Stress*[a] *($10^9 dyn/cm^2$)* As deposited	*After 3-h anneal at 800°C in forming gas*	*After 6-h anneal at 1025°C in forming gas*
Pyrolytic Al_2O_3 (N_2)	+8	+15	
Sputtered Al_2O_3	+0.7	+ 2.7	+5

[a] A negative value indicates a compressive stress and a positive value, a tensile stress.

Sputtered Al_2O_3

Sputtered Al_2O_3 films are in a state of compression on germanium, instead of a state of tension as found for the pyrolytic films. Experience[29] with sputtered SiO_2 suggests that varying the sputtering parameters might alter the stress in the film, but this effect has not been investigated in our work on Al_2O_3.

Heat treatment of the sputtered Al_2O_3 films (see Table 6) causes crystallization and an increase in the stress measured at room temperature. The effect is qualitatively the same as that observed in pyrolytic films, but it cannot be explained quantitatively as thermal mismatch.

Silicon nitride

The silicon nitride films deposited at 800°C are in tension at room temperature and at the deposition temperature. The intrinsic stress in the films at 800°C is at least one order of magnitude greater than that in pyrolytically deposited SiO_2.[28] To be satisfactory for device purposes, the film must be thin enough to avoid both cracking and plastic deformation of the substrate. We are successfully using a 300-Å-thick film that acts as a diffusion mask for gallium at 800°C and does not plastically deform the wafer.

In multilayer films the average stresses appear to be additive from layer to layer.[30] It is possible by judicious choice of film thickness and stress to build up several layers on a substrate so that the net stress at room temperature is very small. One must also ensure that the total stress at elevated temperatures remains smaller than the yield stress of the substrate, as well as smaller than the strength of the film.

Ge surface electrical properties

The Ge-insulator structure is exposed to severe chemical and thermal action during device fabrication steps involving O_2, O_3 and H_2 at temperatures up to 900°C. In addition, high temperature processing in hydrogen, a common diffusion and alloying ambient, is known[31] to produce a high density of surface states on SiO_2-coated Ge surfaces.

Our objective was to develop an insulator film for Ge that has low oxide charge and surface state densities and that is stable during both high temperature fabrication steps and long term exposure to the environment. Because of the known effect of some gases on the surface potential, one primary goal has been to prepare a film that is relatively impermeable to gases.

A variation[31,32] on the usual metal-oxide-semiconductor (MOS) measurement technique was used to measure both the fixed oxide surface charge density and the surface-state density. Capacitance-voltage measurements were made at 77°K so that the surface states could not follow the ac measuring signal, but instead filled and emptied in response to the slowly varying dc bias. All the experimental curves exhibit (1) a flat-band voltage shift, which we have interpreted as due to fixed oxide charge density, and (2) a plateau or approximately constant capacitance region, which we have interpreted[32] as due to a surface acceptor-state density. In the case of hydrogen-annealed SiO_2 films on Ge, we have already shown[31] these midgap acceptor states to be essentially monoenergetic and to lie just above the midgap energy. We have not attempted to determine quantitatively the energy of the acceptor states although, qualitatively, they appear at high concentrations in the center region of the bandgap. By using both n- and p-type samples, it was possible to scan the whole bandgap to within approximately 10 mV of each band edge, and our results are presented in terms of a net fixed surface charge density Q_{fc} and a net surface acceptor-state density N_{ss} for essentially the whole bandgap.

Both n- and p-type samples were used for the measurements, except when processing at 800°C or above would have greatly altered the surface doping of the n-type samples. The films were deposited by the techniques described in Table 1 and were 1500 to 2000 Å thick. In the multilayer structures, 500 to 1000 Å of SiO_2 (O_2) were deposited first, followed by about 2000 Å of Al_2O_3 or about 1000 Å of silicon nitride. All annealing steps were carried out before the deposition of Al field plates and Ge wafer back contacts.

The MOS data for fixed oxide surface charge density Q_{fc} and surface-state density N_{ss} are listed in Table 7 for several films, including the most promising double-layer structures. Additional films studied are included in the following discussion.

- *Single-layer films*

The only film structures that exhibited both low Q_{fc} and low N_{ss} values were those in which the Ge-insulator interface had been exposed in processing to oxygen at about

Table 7 Effect of annealing on properties of the Ge-insulator interface in multilayer film structures.

	Values[b] of Q_{fc}/e and N_{ss}, respectively ($10^{12}/cm^2$)					
Top film	*Initial*		*After 5-min anneal[c]*		*After 15-min anneal[c]*	
SiO_2 (O_2)	2	1.8	−0.3	>13	−0.7	>13
Sputtered SiO_2[d]	0.5	1.2	0.8	1.3	−1.2	9
Al_2O_3 (N_2)	0.7	1	0.5	1	−0.3	1.8
Sputtered Al_2O_3	1	1.4	0.6	1.1	0.4	0.9
Silicon nitride (N_2)[e]	2.1	2.3			2.2	2.3

[a] In each case the underlying film was $SiO_2(O_2)$.

[b] The range of values measured extends about ±50% from the average values listed.

[c] The ambience was forming gas (10% H_2 in N_2) at 700°C.

[d] Only one sample was measured for each entry.

[e] Only data for p-type samples are reported; unexplained irreproducibility was encountered with n-type samples, although one run showed equivalent results.

420°C. In the case of SiO_2 films this exposure was effective if the bare Ge surface was preannealed in O_2 (before the insulator deposition), or if O_2 was used as the insulator deposition ambience [see SiO_2 (O_2) entry in Table 7], or if the film was annealed in O_2 after deposition in H_2.[31] In the case of Al_2O_3 this exposure was effective only if the surface was preannealed in O_2 or if the Al_2O_3 deposition was carried out in O_2. High N_{ss} values were found for Al_2O_3 films deposited in N_2 and for silicon nitride films deposited in N_2 or H_2. These N_{ss} values were not reduced by subsequent annealing in O_2 up to 600°C for 2h. We concluded that the Al_2O_3 and silicon nitride films were relatively impermeable to O_2.

A second important qualitative result was that only SiO_2 (O_2) films were thermally stable with respect to Q_{fc} and N_{ss} on annealing at 700°C in dry N_2. Neither Al_2O_3 nor silicon nitride films were thermally stable at 700°C even though the structures had been preannealed in O_2. That SiO_2 (O_2) films can be annealed at 700°C in dry N_2 with no deleterious effects is important because the alloy emitter formation process takes place at that temperature. However, the increase in N_{ss} and the change to negative Q_{fc} values when the same structure is annealed in forming gas (10% H_2 in N_2), which is used typically in the emitter alloy formation, is undesirable.

- *Multilayer structures*

The single-layer film results suggest the following structure for passivating Ge against H_2 and O_2 permeation and for thermal stability: first, a SiO_2 (O_2) film because the O_2 exposure of the interface keeps both Q_{fc} and N_{ss} low and this film is thermally stable; and second, an Al_2O_3 or a silicon nitride[5] (N_2) film on top of the SiO_2 (O_2) film to prevent further permeation by O_2 or H_2.

Table 7 provides a comparison of Q_{fc} and N_{ss} values between the initial and the hydrogen-annealed multilayer structures. The structures involving Al_2O_3 and silicon nitride are both thermally stable and impermeable to H_2.[32] The data for the sputtered SiO_2-on-SiO_2 (O_2) structure indicate that sputtered SiO_2 is intermediate with respect to H_2 permeability between SiO_2 (O_2) and the Al_2O_3 or silicon nitride films.

The multilayer structure using Al_2O_3 or silicon nitride (N_2) is recommended for device usage. In the Ge planar technology[4] this structure can be used to advantage as the so-called "second oxide," since it will act as a diffusion barrier to H_2 for at least 5 min at 700°C, which is approximately the ambient exposure during the emitter alloy cycle. Some preliminary data indicate that approximately 2000 Å of sputtered Al_2O_3 or 1000 Å of silicon nitride are an adequate mask against H_2 diffusion at 700°C for up to 1h.

Temperature-bias stressing

The electrical surface conditions that are established by an appropriate annealing treatment must remain constant during the life of the device. The performance of circuits containing field-effect devices can be affected by changes in surface charge density of the order of 10^{11} e/cm^2 (e is the magnitude of the electron charge). Bipolar transistors are somewhat less sensitive, and shifts up to 10^{12} e/cm^2 may be tolerable. The electric fields that exist during normal device operation can alter the surface charge density beyond these limits if mobile ions are present in the oxide (e.g., the well-known Na^+ effect), if the dielectric film is polarizable, or if trapping sites exist in the insulator near the semiconductor interface. Electrical stability of the Ge surface under the various insulating films was evaluated by subjecting the MOS structure to fields of $\pm 5 \times 10^5$ V/cm at 150°C and observing the resultant change in the capacitance-voltage (CV) characteristic. The amount of mobile ionic charge was measured directly by monitoring the charge transported during stressing.

The effects of temperature-bias stressing are given in Table 8; while there is some variability among samples, the measured values for most devices fall within a factor of two of the values cited. Changes in fixed charge density as determined by the CV measurements are listed in the second column; for SiO_2 films these changes indicate ion motion. Although positive stress bias may cause a larger effect than negative stress bias, the difference is within the variability factor of two; therefore only a single value, representative of both stress polarities, is given.

The changes in Q_{fc} for the Al_2O_3 and Al_2O_3-over-SiO_2 films are significantly smaller than for SiO_2 alone and reflect the improved electrical stability previously reported for Al_2O_3.[14] These small shifts can be in either direction for either bias polarity. This ambiguity in direction has been

Table 8 Charge stability of insulating film-Ge structures after electrical-bias stressing.

Film	*Charge transport* $(10^{12}e/cm^2)$[a]	*Change in* Q_{fe} *due to stress*[b] $(10^{12}e/cm^2)$
SiO_2 (H_2)		2
SiO_2 (H_2 dens)	3	1
SiO_2 (O_2)		2
Al_2O_3 (N_2)	0.7	0.4
Al_2O_3 (N_2) over SiO_2 (O_2)	0.9	0.3
Sputtered Al_2O_3 over SiO_2 (O_2)		0.3

[a] The magnitude of the electronic charge is denoted by *e*.
[b] See text for discussion of direction change.

explained[14] as due to the combined presence of a trapping instability at the Ge-insulator interface and a mobile ion instability in the film. The magnitude of the ion-motion effect is reduced by the presence of Al_2O_3 to a level comparable with that of the trapping; the net effect depends on which mechanism dominates in the particular device.

A comparison of the changes in Q_{fe} with the charge transport data in Table 8 shows that more charge is transported during stressing than is detected by the CV shift. Measurements of both quantities on the same device have established that the charge transport in SiO_2 (H_2 dens) is from two to four times larger than the associated CV shift. This discrepancy, which has been observed only for Ge devices, contrasts with the good agreement between charge transport and CV shift found by Kerr[33] for thermal SiO_2 and by us for SiO_2 (H_2 dens) deposited on silicon. The model of combined presence of trapping at the Ge-SiO_2 interface and ion motion in the film provides an explanation of the difference between charge transport and CV shift.[14]

The factor-of-two variability in both the magnitude of the CV shift and the amount of charge transported during stressing in supposedly identical samples probably reflects differing contamination of the films or of the Al field plates. The fact that the Al_2O_3 effectively blocks ion motion in the Al_2O_2-SiO_2 structures suggests that the source of mobile ions causing the large charge transport in single-layer SiO_2 films is associated with the Al field plate evaporation.

Although we did not study the effects of contaminants, a few samples of undensified SiO_2, which had been deliberately Na-contaminated with a NaOCl solution or which had been used as masks in As diffusion, were subjected to temperature-bias stressing. The Na-contaminated devices showed much larger CV shifts in a direction consistent with an ion motion mechanism than did the untreated samples; the charge transport measurements showed about 2×10^{13} mobile ions/cm^2, which corresponds to the amount of Na shown by radio tracer work[34] to be absorbed by pyrolytic SiO_2 from NaOCl. We noted a factor-of-two decrease in stability after As diffusion at 700°C, which indicates that As in SiO_2 gives rise to some mobile charge. The extent of this mobility (or the amount of As retained), however, probably depends on the state of densification of the oxide. Films used to mask a 750-°C As diffusion showed no adverse change in stability, presumably because of densification during the higher temperature diffusion process, which blocked the transport of the mobile species.

Summary

Aluminum oxide and silicon nitride have considerable advantages over silicon dioxide for application as passivating and masking films for Ge planar transistor technology. Sputtered Al_2O_3 was found to be the best film from an over-all point of view and considerably superior to both pyrolytic Al_2O_3 and silicon nitride in some properties.

More specifically, silicon nitride and Al_2O_3 were found to be impermeable to water under high humidity storage conditions, while SiO_2 films were quite susceptible to water pickup (which depends on deposition conditions). In addition, Al_2O_3 and silicon nitride act as H_2 and O_2 diffusion masks, which is important in Ge technology because of the H_2-induced surface-state formation on Ge at high temperature. The best passivating film structures consist of Al_2O_3 or silicon nitride with an underlayer of low temperature SiO_2. The underlayer of SiO_2 is necessary to achieve low fixed charge and surface-state densities. The results of electrical- and temperature-bias stressing of Al_2O_3 and silicon nitride films, either singly or in combination with SiO_2, also indicate the superiority of these films over SiO_2 alone.

Silicon nitride, in our experiments, was the best and apparently only satisfactory diffusion mask against Ga at 800°C for long times, although Al_2O_3 and aluminosilicate films had some masking capability at 800°C.

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