Interaction Between Ti and SiO_2

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ABSTRACT

We have investigated the interaction between Ti and SiO_2 in the temperature range of 400° to about 1000°C. The reaction proceeds in a layer-by-layer fashion and consists of SiO_2 reduction followed by the formation of a Ti-rich silicide at the interface. At higher temperatures, a Ti-rich oxide is formed near the surface. The reaction starts at approximately 400°C, and the loss of SiO_2 becomes significant above 500°C. A strong interaction between Ti and SiO_2 takes place at 700°C and above. The thicker the SiO_2, the higher resistance it has to degradation due to elevated temperature effects.

The performance and density of today's MOS integrated circuits are further improved by scaling down the physical dimensions of the individual circuit elements. It follows from the MOS scaling laws that the miniaturization process reduces the length of interconnect lines by the scaling factor and their cross-sectional area by the square of that factor. Consequently, the resistance of polycrystalline silicon lines increases with the scaling factor. However, the area of ohmic contacts is reduced by the square of the scaling factor, which results in an increase of the contact resistance by the square of that factor. The above resistance increases give rise to excessive RC time constants and IR voltage drops which may offset the speed advantages gained by scaling the MOS technology to smaller feature sizes.

Recently, refractory metals and their silicides have found an increased interest as means to reduce both the contact resistance and the high resistance of poly-Si lines and diffusion layers. Specifically, VLSI technology makes use of Ti in contact structures (1, 2) and self-aligned $TiSi_2$ in both source/drain and gate areas (3, 4). If Ti is employed in oxide windows for ohmic contacts and Schottky diodes, it is likely to be in connection with the field oxide as well. However, any reaction between Ti and SiO_2 during postmetal annealing at 400°-450°C could degrade the device performance. However, self-aligned $TiSi_2$ over poly-Si lines and diffusion layers is formed at higher temperatures, around 600°-700°C. The unreacted Ti over the field oxide is removed in a subsequent step. Any residue on the oxide as a result of the interaction of Ti with SiO_2 during self-aligned $TiSi_2$ formation presents a potential hazard to the performance of the device. Therefore, the Ti/SiO_2 interaction has to be minimized. For this purpose, it is imperative to study the interaction between Ti and SiO_2.

The reactions of thin films of Ti, V, and Nb with SiO_2 substrates was first investigated by Kräutle *et al.* (5). They found that, upon annealing a Ti film on SiO_2 at 800°C for 2h in vacuum, a bilayer structure is formed, consisting of a surface layer of Ti with about 50% oxygen and a layer beneath of mostly Si and Ti in the ratio Si:Ti = 0.62. They were unable to identify the compounds formed. Our goal was to study in detail the interaction between Ti and SiO_2 in order to determine its implications on device performance. For that purpose, we carried out both thin film analysis and electrical measurements on MOS capacitors. The results of this paper extend very well those of two recent photoelectron spectroscopy studies on low coverages of Ti and SiO_2 to the case of thin films, as they are used in integrated circuits.

Experimental

The Si substrates used in this work were <100> oriented and p-type doped. A 1000Å thick SiO_2 layer was grown on 10 Ω cm Si substrates in a dry-wet-dry oxidation sequence at 1000°C with HCl addition to the oxygen gas. Thinner SiO_2 layers up to 350Å were grown on 2 Ω cm material in dry oxygen with HCl addition. Blanket layers of 1000Å Ti were evaporated in a diffusion-pumped system from a resistively heated source. The base pressure prior to evaporation was better than 2×10^{-7} torr, and the evaporation rate was 10 Å/s. During evaporation, the substrates were maintained at a temperature of 150°C. Titanium MOS capacitors were prepared by evaporating circular Ti dots of 0.8 mm diam through a metal mask.

Samples of the blanket-deposited wafer as well as of the MOS capacitors were subsequently annealed for various times at temperatures ranging from 400° to about 1000°C in Ar. The Ar gas was purified in a hot Ti sponge filter prior to purging of the annealing furnace. The thin films were analyzed with Rutherford backscattering spectrometry (RBS) (6) and glancing angle x-ray diffractometry. Both leakage current and C-V measurements were used in the investigation of the Ti-MOS capacitors.

Other samples of the blanket-deposited wafer were first annealed at temperatures between 500° and 800°C and then stripped of the unreacted Ti in an etching solution which attacks neither titanium silicide nor SiO_2 (7). The thickness of the remaining SiO_2 layer was then measured with optical interferometry. Finally, SIMS analysis was used to determine a possible Ti diffusion into the SiO_2.

Results

Thin film analysis.—A set of samples with 1000Å Ti on 1000Å SiO_2 was annealed for 30 min in 100°C steps from 400° to about 1000°C. The RBS spectra of these samples are summarized in Fig. 1. From this figure, it is clearly seen that the Ti signal is well separated from the Si signal, whereas the oxygen signal is superimposed on the Si signal. This is due to the difference in atomic mass of these elements. The energies for scattering of the $^4He^+$ particles from surface positions of the elements are indicated by the vertical arrows marked Ti, Si, and O.

The spectra for the as-deposited sample and the samples annealed up to 600°C are practically identical and

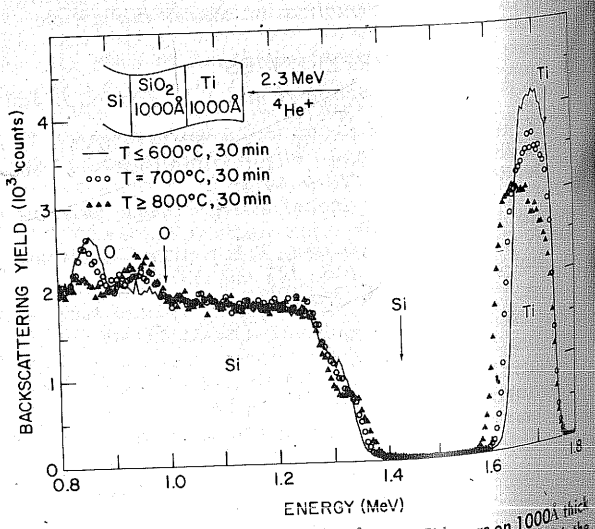

Fig. 1. 2.3 MeV $^4He^+$ spectra of 1000Å thick Ti layers on 1000Å thick SiO_2 annealed under various conditions. The vertical arrows mark the surface position of the corresponding elements.

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represented by the solid line in Fig. 1. The oxygen and silicon signals of the SiO_2 layer are displaced to energies below their corresponding surface position because of the energy loss of the $^4He^+$ particles in the overlaying Ti film. Diffusion of Ti into the SiO_2 is not observed under these annealing conditions. Upon annealing at 700°C, two changes in the RBS spectrum (open circles) can be discerned. First, the height of the Ti signal has dropped and a second oxygen peak near the surface position of oxygen has appeared. This indicates that a significant amount of oxygen has dissolved in the Ti film. Second, the width of the Ti signal has increased and the Si signal extends now to higher energies. This signifies that Ti and Si at the original Ti/SiO_2 interface have reacted with each other and formed a mixed layer. Heat-treatments at 800°C and higher yield RBS spectra typical of the one represented by the filled triangles in Fig. 1. It is clearly seen that most of the oxygen from the SiO_2 layer is now distributed in the Ti layer and that the Ti and the Si have mixed extensively. Finally, we find from Fig. 1 that within the accuracy of RBS the area under the oxygen peaks is preserved, indicating that the oxygen in the Ti layer originates mainly from the decomposed SiO_2 layer.

Strong interactions occur between the Ti and the SiO_2 at high temperatures. This is demonstrated in Fig. 2, which shows the RBS spectrum of a sample annealed at 900°C for 30 min. It is apparent fom the step in the Ti signal at 1.7 MeV in Fig. 2 that the original SiO_2/Ti structure has been transformed into a different bilayer structure. The uppermost layer contains Ti and O_2 in the ratio Ti:O = 2:3. This can be inferred from the heights of the Ti and O signals near their surface positions. In a similar fashion, we can determine the composition of the layer beneath. It consists mostly of Ti and Si in the ratio of Ti:Si = 5:3. A thin interfacial layer of the original SiO_2 remains between the Ti-Si mixed layer and the Si substrate, as indicated in Fig. 2. The drop of the oxygen signal between the surface position "s" and interface position "i" indicates that the Ti-Si mixed layer contains only a small amount of oxygen.

We used glancing angle x-ray diffraction to identify the compounds formed in the interaction between Ti and SiO_2. Figure 3 shows the diffraction spectrum of a sample which has been annealed at 800°C for 30 min. Most of the diffraction lines can be ascribed to two compounds, Ti_5Si_3 or Ti_5Si_4, with the exception of one line which can only be identified as the (121) diffraction of Ti_5Si_3. Thus, we conclude from the x-ray analysis that the compound formed is the metal-rich silicide Ti_5Si_3. This result is in excellent agreement with the composition of the compound determined by RBS. The result is also in good agreement with the atomic ratio of Si and Ti reported by Kräutle *et al.* (5).

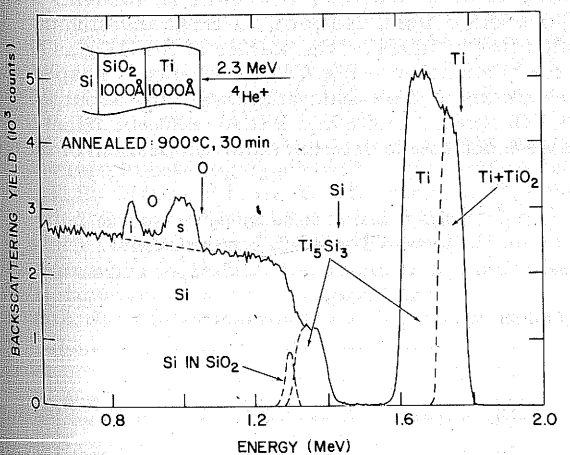

Fig. 2. 2.3 MeV $^4He^+$ RBS spectrum of a Si/1000Å SiO_2/1000Å Ti sample following a heat-treatment for 30 min at 900°C. The contributions of the various compounds to the overall spectrum is indicated by the dashed lines, and the vertical arrows mark the surface positions of the corresponding elements.

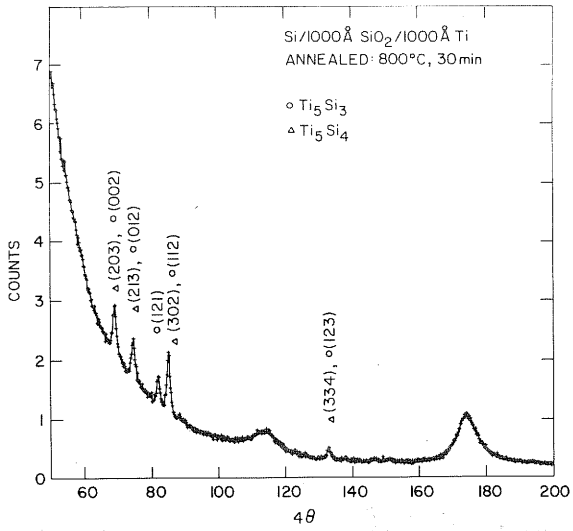

Fig. 3. Glancing angle x-ray diffraction pattern obtained with Cu K α radiation from a Si/1000Å SiO_2/1000Å Ti sample after annealing for 30 min at 800°C, identifying the compound Ti_5Si_3. The broad diffraction peaks are artifacts of the x-ray equipment.

The broad diffraction peaks in Fig. 3 are artifacts of the x-ray equipment.

We cannot identify the Ti-oxide phase from the x-ray spectra of Fig. 3. The number of diffraction lines we obtained from this as well as other samples is insufficient to determine which of the many possible Ti-oxide compounds are formed. From RBS analysis alone one would speculate that Ti_2O_3 is the compound in question. However, we believe that in this temperature range rutile TiO_2 is formed in the presence of some unreacted Ti.

MOS capacitor measurements.—The breakdown voltage of the Ti-MOS capacitors prepared with a 1000Å thick Ti layer was measured before and after various heat-treatments. We defined the breakdown voltage as the voltage at which the leakage current surpassed 50 μA. The histograms of the capacitors as a function of breakdown voltage for oxide thicknesses of 100, 200, and 350Å are shown in Fig. 4. Histograms are shown before any heat-treatment of the capacitors and after a maximum permissible time-temperature cycle that the capacitors were able

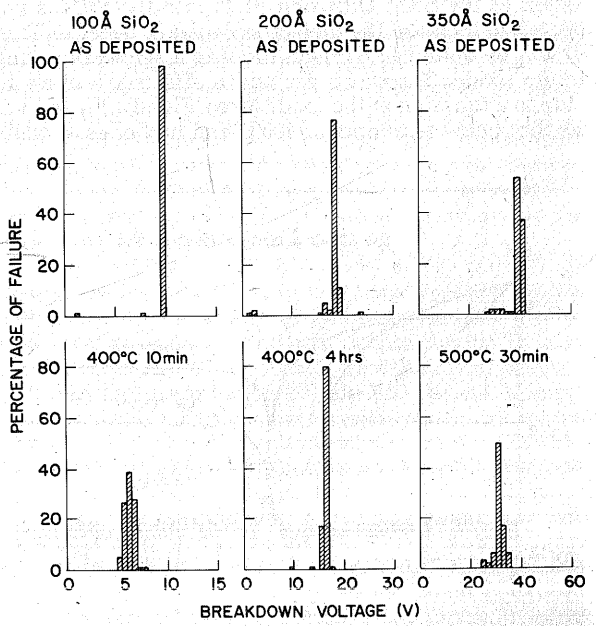

Fig. 4. Distribution of Ti-MOS capacitors as a function of breakdown voltage for oxide thicknesses of 100, 200, and 350Å. Distributions are shown before and after a heat-treatment at 400° and 500°C, respectively.

to withstand: namely, 10 min at 400°C for 100Å SiO_2, 4h at 400°C for 200Å SiO_2, and 30 min at 500°C for 350Å SiO_2. Two features are apparent from Fig. 4. First, the width of the distributions is small and is not altered in a marked way by the annealing process. This indicates that the integrity of the MOS structure is maintained. Second, the breakdown voltage is shifted to lower voltages after the annealing process. This points to either a thinning of the SiO_2 layer and/or increase of the dielectric constant of SiO_2. We could not measure the breakdown voltage for thicker oxide layers because the voltage was too high for our instrumentation. In this case, we measured only the leakage current.

The leakage current of Ti-MOS capacitors with 1000Å thick oxide layer is stable for heat-treatments of 30 min up to 600°C. This is shown in Fig. 5, which illustrates the dependence of the leakage current of a typical capacitor on applied bias. The small peak at 0 V is due to charging of the capacitor. After a heat-treatment of 30 min at 700°C, a pronounced increase in leakage current is observed on some of the capacitors. The I-V characteristic differed strongly from one capacitor to another upon annealing at 700°C. An example is shown in Fig. 5. It seems that the capacitor is about to fail at that temperature. However, after annealing the capacitors for 30 min at 800°C and above the I-V characteristics turned out to be consistent among the capacitors investigated. A typical example is shown in Fig. 5. The asymmetry of the leakage current on the polarity of the applied bias is remarkable and is indicative of a rectifying behavior. We believe that in this temperature range the Ti has completely decomposed the oxide layer, thereby destroying the MOS capacitor and forming a low barrier Schottky diode with the Si substrate. Titanium-MOS capacitors prepared on 350Å thick oxide layers were destroyed after a heat-treatment at 600°C for 30 min.

We have also investigated the Ti-MOS capacitors with C-V measurements. The high frequency (1 MHz) C-V characteristics of capacitors with a 350Å thick oxide layer are shown in Fig. 6. The C-V characteristics are well behaved for as-deposited capacitors and capacitors which have been annealed for 30 min up to 500°C. However, it is obvious from Fig. 6 that the capacitance in accumulation increases with increasing annealing temperature. In addition, a reduction in flatband voltage is noticeable in Fig. 6 upon annealing of the capacitors, in accordance with the increase in accumulation capacitance. Both effects can be explained by a thinning of the oxide layer due to Ti-SiO_2 interaction and/or an increase of the dielectric constant of the SiO_2. Diffusion of Ti into the SiO_2 is not expected to increase the dielectric constant because Ti in SiO_2 will be bound to oxygen, forming a semiconducting titanium oxide. Therefore, the above effects are likely to be due to a thinning of the oxide layer. Finally, Fig. 6 indicates that heat-treatments of 600°C and higher essentially

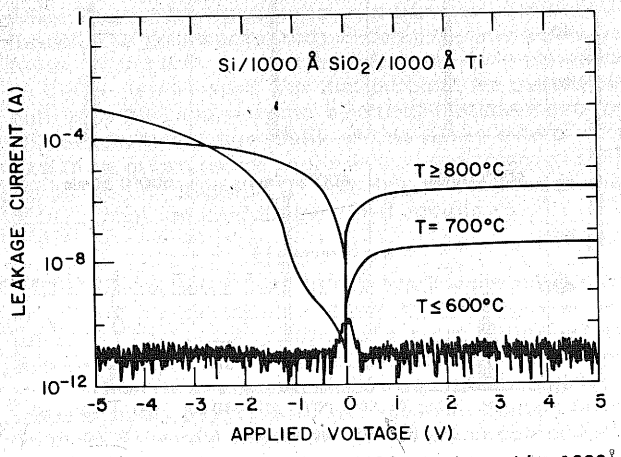

Fig. 5. Leakage current vs bias for Ti-MOS capacitors with a 1000Å thick oxide layer following heat-treatments for 30 min at various temperatures. Note the asymmetry of the I-V characteristic on the polarity of the applied bias.

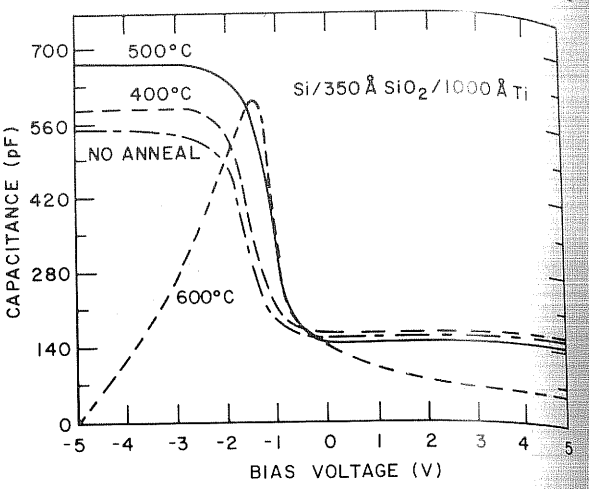

Fig. 6. High-frequency (1 MHz) C-V characteristics of Ti-MOS capacitors with a 350Å thick oxide before and after annealing for 30 min at various temperatures. Note the change in accumulation capacitance and flatband voltage with annealing temperature.

short the MOS capacitors prepared with a 350Å thick oxide layer. For MOS capacitors prepared with a 1000Å thick SiO_2, shorting occurred during heat-treatments at 700°C.

Investigations of the oxide layer.—So far, it seems that the electrical properties of the oxide layer beneath the titanium silicide are not altered by the Ti-SiO_2 interaction. The steep trailing edges of the Ti signals in the RBS spectra of Fig. 1 and 2 indicate that the silicide-oxide interface is sharp. In addition, a noticeable Ti diffusion into the SiO_2 has not been observed with RBS. To further substantiate these facts, we have investigated the properties of the oxide layer beneath the reaction interface in detail.

First, we measured the thickness of the SiO_2 layer after the interaction between Ti and SiO_2. For that purpose, we annealed Ti films on SiO_2 at temperatures between 500° and 800°C. The unreacted Ti was then etched away (3), and the thickness of the remaining oxide was measured with optical interferometry. Table I lists the amount of oxide consumed by the Ti-SiO_2 interaction for various annealing conditions. It is clear from Table I that the amount of SiO_2 lost depends on both annealing temperature and time. The amount of SiO_2 lost during the 500°C heat-treatment corresponds to the increase of the accumulation capacitance at 500°C, as shown in Fig. 6. For annealing temperatures of 700°C and above, the SiO_2 surface acquires a metallic luster and the measurement of the loss of SiO_2 with optical interferometry became difficult. We tried to analyze the nature of the metallic luster with ESCA, but were unable to detect foreign elements within its resolution limit. However, a SEM investigation revealed tiny residues on the surface of the SiO_2, as shown in the micrograph of Fig. 7. The spherically shaped residues are about 300Å diam and cover only about 0.5% of the SiO_2 surface. Therefore, ESCA could not detect them. We were not able to determine the composition of the res-

Table I. Loss of oxide during the reaction between Ti and SiO_2 in argon ambient

Heat-treatment		Loss of oxide (Å)
Temperature (°C)	Time (min)	
500	30	55
550	30	90
550	60	105
550	90	110
550	120	115
600	30	150
700	30	*
800	30	*

* Sample surface exhibits metallic luster.

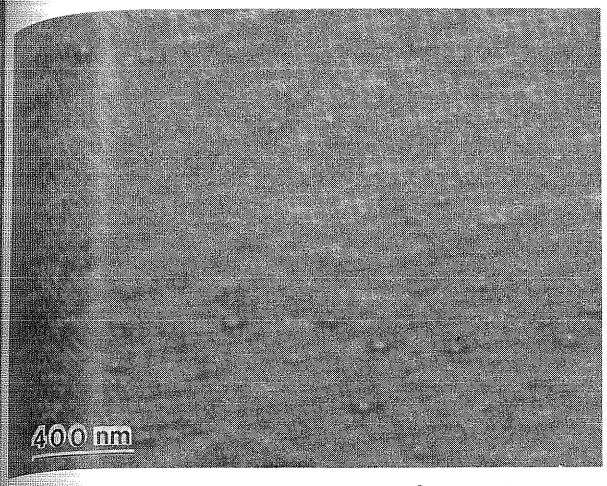

Fig. 7. SEM micrograph of a Si/1000Å SiO_2/300Å Ti sample following heat-treatment for 30 min at 800°C and stripping of the Ti-silicide on unreacted Ti. A thin Au layer has been evaporated to prevent charging up of the SiO_2 Layer.

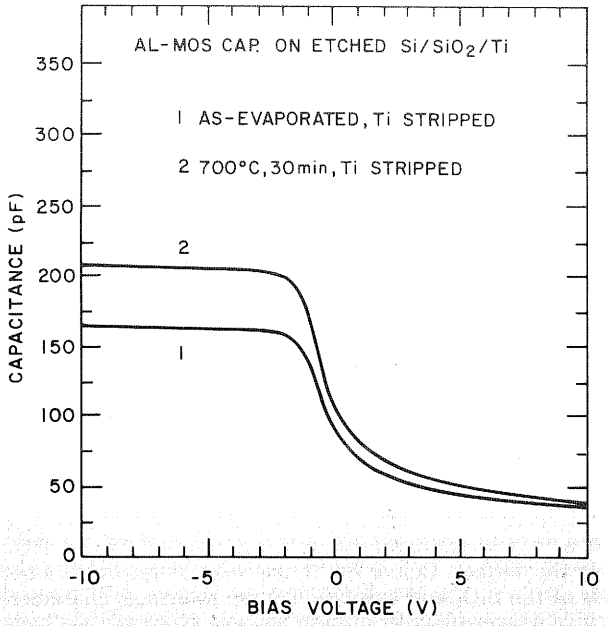

Fig. 8. High-frequency (1 MHz) C-V characteristics of Al-MOS capacitors fabricated on etched Si/SiO_2/Ti substrates. Two cases are shown, one for substrates with Ti stripped after evaporation and one for substrates with Ti stripped after reaction with SiO_2 at 700°C for 30 min.

idues. It is possible that they consist of a metal-rich titanium silicide such as Ti_5Si_3 because they were not removed by the selective etching solution.

The loss of SiO_2 during interaction between Ti and SiO_2 is consistent with the RBS profiles of oxygen shown in Fig. 1 and the increase of the accumulation capacitance observed in Fig. 6. These facts rule out Ti diffusion into the SiO_2. We also performed SIMS analysis of the SiO_2 layer after stripping of the Ti-silicide to further support the absence of Ti diffusion. The analysis revealed that a possible Ti concentration in the SiO_2 must be below the sensitivity of SIMS for Ti ($< 10^{15}$ cm^{-3}).

Finally, we have prepared Al-MOS capacitors on 1000Å thick SiO_2 layers which had been reacted with the Ti at 700°C for 30 min and subsequently stripped of the silicide and any unreacted Ti. For comparison, we have also prepared Al-MOS capacitors on unreacted SiO_2 layers. The thickness of the Al dots was 7000Å. The high frequency (1 MHz) C-V characteristics of the capacitors, which are shown in Fig. 8, are well behaved in both cases, irrespective of the 700°C heat-treatment. The accumulation capacitance for the capacitors on reacted SiO_2 is 50 pF higher than for those on unreacted SiO_2. This corresponds to a reduction of the oxide thickness of about 200Å, which is in good agreement with the observed oxide loss given in Table I. Thus, we are confident to rule out Ti diffusion into the SiO_2 during the heat-treatments.

Discussion

It is observed in general that the interactions between thin films of refractory metals and plain Si substrates yield silicon-rich silicides. In the case of Ti films on Si, the formation of the monosilicide TiSi is observed around 500°C and the disilicide $TiSi_2$ is formed at 600°C or higher temperatures (7). This is in contrast to the present results of the interaction between Ti and SiO_2. Here, a metal-rich silicide, Ti_5Si_3, is formed at the Ti-SiO_2 interface. The silicon needed for the silicide formation originates from SiO_2, which is decomposed by the Ti-SiO_2 interaction. The oxygen which is freed by this interaction is dissolved in the Ti and at higher temperatures reacts with the Ti to form an oxide layer near the surface. The oxide layer is metal rich and consists presumably of TiO_2 and unreacted Ti.

These conclusions are in basic agreement with those presented by Kräutle *et al.* (5). However, our investigation of Ti-MOS capacitors revealed the onset of the Ti-SiO_2 interaction at 400°C, which is below the temperature for conventional Ti-silicide formation. Kräutle *et al.* (5) claimed that refractory metals react with SiO_2 at temperatures which are about 200°C higher than the temperature to form the corresponding silicide with Si. This discrepancy is not surprising because their methods of analysis were restricted to RBS and x-ray diffraction. As shown in Fig. 1, RBS does not detect any interaction between Ti and SiO_2 below 600°C. There is also a remarkable analogy between the interaction of Ti and SiO_2 and that of Ti and Si_3N_4. Borisov *et al.* (18) reported that mixtures of Ti and Si_3N_4 powders reacted at temperatures below 1330°C to form Ti_5Si_3 and TiN compounds.

It seems that the Ti-SiO_2 interface is a very reactive one. Titanium atoms at the interface have a strong tendency to reduce neighboring Si-O bonds and to form new Ti-O and Ti-Si bonds. At this point, it is instructive to compare our results with the findings of two recent photoelectron spectroscopy investigations of the Ti/SiO_2 interface (9, 10). It is reported that the presence of SiO_2 at the Si surface has a significant effect on the reaction of Ti and Si, and, more important, that the thickness of the SiO_2 determines the end products of the reaction. The evaporation of Ti onto thin layers (< 20Å) of SiO_2 at room temperature was found to break Si-O bonds and to rebond the free oxygen atoms to Ti atoms (10). This reactivity of the Ti is reflected in its excellent adhesion to insulators, in particular SiO_2 and Si_3N_4. The formation of silicides is not observed during evaporation of Ti onto SiO_2. Annealing at moderate temperatures (300°-400°C) changes the bonding of the Ti from Ti-O to Ti-Si and produces a stable silicide phase. For thin oxide layers, the silicide is similar to that formed with a clean Si substrate (9, 10).

It is the combination of both processes, the reduction of SiO_2 and the low temperature interfacial reaction with Si, which mark the reliability of Schottky barriers and the low resistivity of ohmic contacts prepared with Ti. However, the reactivity of the Ti/SiO_2 interface is a disadvantage when the preservation of thin SiO_2 layers is important. This is specially the case for gate oxides and regions of thinner field oxide around device oxide windows. Heat-treatments above 400°C cause a noticeable reduction of the oxide thickness, owing to the Ti-SiO_2 interaction. The excess oxygen probably forms a solid solution with the unreacted Ti. As the Ti-SiO_2 reaction proceeds during extended or higher temperature heat-treatments, the oxygen concentration in the Ti increases. When it exceeds the solid solubility limit, a Ti-rich oxide forms, in agreement with the photoelectron spectroscopy results of Ti on thick SiO_2 layers (9).

We have not found any indication of Ti diffusion into the SiO_2 during heat-treatments up to 800°-900°C. The

photoelectron spectroscopy studies of the Ti/SiO_2 interface (9, 10) were also unable to detect diffusion of Ti beyond the mixed interfacial layer amounting to a few monolayers. Thus, we conclude that the diffusivity of Ti in SiO_2 is very low. This is also expected from the fact that Ti is very reactive and reduces quickly many oxide compounds. As a consequence, the interface between evaporated Ti and SiO_2 is very sharp and stays relatively sharp during subsequent heat-treatments up to 700°C. This is beneficial to the application of Ti in the manufacture of integrated-circuit elements.

Conclusions

We have studied the interaction between Ti and SiO_2 during thermal annealing in the temperature range of 400° to about 1000°C. The results show that Ti reacts in a limited fashion with SiO_2 at temperatures of 700°C and below, but strong interactions take place at higher temperatures. At high temperatures, the reaction mechanisms consist of the decomposition of SiO_2 by the Ti metal and the formation of a Ti-rich silicide, Ti_5Si_3, at the interface and a Ti-rich oxide, presumably a mixture of Ti and TiO_2, near the surface. Below 700°C, the reaction results in a net loss of the SiO_2 and exhibits a sharp interface, characteristic of a layer-by-layer growth process. However, we have not observed diffusion of Ti into the SiO_2 during the interaction.

The application of a Ti-based metallurgy to silicon devices requires special attention. The use of Ti or Ti silicides in contact structures and interconnects should be of no concern as long as the oxide thickness is greater than 350Å and the post-metal heat-treatment is performed at a temperature not exceeding 400°-450°C. However, in the case of self-aligned $TiSi_2$, the formation temperature of the silicide should be kept below 700°C in order to prevent excessive Ti-SiO_2 interactions. Also, the field oxide should have a thickness of at least 1000Å. Besides these restrictions, which are not severe at all, there is no reason why the full advantage of the application of Ti or Ti-silicide metallurgies to device manufacturing cannot be taken.

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Low Energy Proton Beam Lithography with a Thin Oxygen-Etch Barrier Layer

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ABSTRACT

Low energy protons in the several keV energy range have very limited penetration depths into polymer films. This limitation necessitates the use of very thin oxygen-etch barrier layers and of dry image development by oxygen reactive ion etching. For negative tone images, the etch-barrier layers were deposited patternwise by proton-beam-induced polymerizations of organo-metallic compounds, followed with dry image development by oxygen reactive ion etching. For positive tone images, the etch-barrier layers were deposited (prior to patternwise exposure to proton beams) on top of polymer films by plasma polymerizations of organo-metallic compounds, or by evaporation or sputtering of certain metals. Hydrogen atoms and/or protons react with metal atoms in the etch barrier layers to yield volatile metal hydrides, making the exposed areas more vulnerable to oxygen reactive ion etching, and providing positive tone images after image development. Sub-keV electrons can replace low energy protons for fabrications of positive-tone polymer images. In these processes, almost any kind of carbonaceous polymer film can be used as the imaged material. With a bright ion gun available, the exposure times could be less than a second, yielding high aspect ratio and high resolution polymer patterns.

Ion beam lithography does not suffer from the proximity effect, which is one of the most serious problem of electron beam lithography with electron energy of 20-30 keV (1). The very limited penetration depths of ions, however, require high acceleration energies of ions (for example, 150 keV proton beams), to be useful for lithographic applications (2). Associated with high energy ion beams, there are many problems to be considered. With the use of very thin oxygen etch barrier layers deposited from the vapor phase, as in plasma polymerization or by sputtering or evaporation, a few keV proton beams can be utilized successfully to delineate high resolution positive-tone polymer images, as described later.

Shallow ion implantation [gallium ion (3), indium ion (4), silicon ion (5)] into resist films has been reported to fabricate negative-tone polymer images. An organic semiconductor film was used to avoid charge buildup with scanning indium ion (4). In all these shallow ion implantations for reducing oxygen plasma etch rates, high doses of ion beams (1×10^{15} Si ion/cm^2) are required to obtain reasonably thick polymer images. In a similar way as in ion implantations, thin oxygen-etch barrier layers can be

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