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ELECTRICAL PROPERTIES OF SPUTTERED AlN FILMS AND INTERFACE ANALYSES BY AUGER ELECTRON SPECTROSCOPY

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AlN films were deposited at room temperature by reactive sputtering. Silicon surfaces, AlN films and AlN–Si interfaces were analysed by Auger electron spectroscopy. The effects of ion and chemical silicon substrate etchings and the effects of AlN post-deposition annealings on the aluminium, nitrogen, silicon, oxygen and carbon depth profiles, especially in the interface region, are discussed. Leakage currents and *C–V* characteristics of the metal–AlN–Si structures were determined. The dielectric constant of AlN was 11.3 ± 0.5 at 1 MHz and the density of fixed interface charges varied between $+2.5 \times 10^{11}$ and -5×10^{10} cm^{-2}. Oxygen and positive fixed charges induced at the AlN–Si interface by the native SiO_2 layer on the silicon substrate were removed by annealing at 650 °C. This study showed that the electrical characteristics were improved when the native SiO_2 was not etched before the deposition of AlN.

1. INTRODUCTION

AlN is a dielectric and refractory III–V compound used as an insulator in some MIS structures. AlN films have been deposited by chemical vapour deposition[1-4], ion implantation[5] and reactive sputtering[6,7]. The thermal stress and the subsequent surface state density at the insulator–semiconductor interface[8] should be minimized by deposition at a low temperature. Relationships between electrical properties and silicon surface treatments before AlN deposition have not yet been established[9]. The composition and the states present at the insulator–semiconductor interface are likely to be affected by semiconductor surface treatments and by AlN post-deposition annealings. The purpose of this study was to investigate the AlN films deposited at room temperature by reactive sputtering and to demonstrate the feasibility of producing MIS structures with low fixed charge densities at the AlN–Si interface and with stable electrical characteristics. In this work various silicon surface treatments were performed before deposition of AlN films. The surfaces of the silicon substrates and the AlN–Si interfaces were analysed by Auger electron spectroscopy (AES). *I–V* and *C–V* characteristics of the metal–AlN–Si structures were then determined before and after annealing. Relationships between the electrical characteristics of the MIS structure and the composition of the AlN–Si interface are established and discussed in this paper.

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2. EXPERIMENTAL PROCEDURES

For this work n-type (111) silicon wafers with a phosphorus concentration of 10^{15} atoms cm^{-3} were used. These wafers were degreased in trichlorethylene and rinsed in ethanol prior to ion etching or chemical treatment. The ion etching before AlN deposition was performed *in situ* with low energy (100 eV) argon ions (Ar^+); the ionic current density was about 150 μA cm^{-2}. The ion etching rate deduced by weighing the silicon wafer was about 20 Å min^{-1}. The etching times were between 2 and 60 min. The different chemical treatments are given in Table I. Reactive sputtering of the aluminium target was always performed at room temperature in an N_2–Ar gaseous mixture; the nitrogen content and optimal pressure of this mixture were 12% and 2×10^{-3} Torr respectively. The d.c. triode system avoided the undesirable bombardment of the sample surface by electrons and ions during deposition[7]. The deposited films were confirmed to be AlN by an X-ray diffraction technique and by Rutherford backscattering spectroscopy. Oxygen traces were present as an impurity; the atomic ratio O/N was always less than 1%[7]. The post-deposition heat treatments in a reducing atmosphere were carried out in order to decrease the surface state density and to study the thermal stability of the AlN–Si interface. The sample was placed in a fused silica tube in which a mixture of hydrogen (5%) plus argon was flowing. The temperature was maintained in the range 350–650 °C for 1 h.

TABLE I

DIFFERENT SPECIMENS AND THEIR TREATMENTS BEFORE AES ANALYSIS

Analysis type	*Specimen*	*Silicon substrate treatment*	*Approximate thickness of deposited AlN film* (Å)
AlN–Si interface	A	Untreated	100
	B	Etched by Ar^+ ion bombardment	100
	G	Untreated	150
	H	Annealed at 500 °C after AlN deposition	150
Silicon substrate surface	F	Etched[b] and cleaned[c]	
	E	Boiled[a], etched[b] and cleaned[c]	
	D	Boiled[a] and cleaned[c]	
	C	Cleaned[c]	

[a] In 70% HNO_3 for 15 min.

[b] In buffered HF for 30 s.

[c] In deionized water (boiling for 15 min and rinsing ten times before drying).

AES analyses were performed in an ultrahigh vacuum system ($P < 10^{-9}$ Torr) with a chamber for the rapid introduction of specimens. The analyser was a low energy electron diffraction and Auger spectrometer with four grids and a coaxial electron gun. The primary electron energy and current were 1000 eV and 1 μA respectively. Ion milling was performed with low energy argon ions (400 eV, 1.5 μA cm^{-2}) and the milling rate was about 0.8 Å min^{-1}. The entire Auger spectrum was recorded at several points on each specimen at different stages of ion milling. The peak-to-peak amplitudes of $dN(E)/dE$ in arbitrary units were used to obtain depth distribution profiles. Each constituent has its own characteristic sputtering rate during ion milling. The composition of the analysed surface is thus different to the underlying composition. The concentration of each constituent is changed at the surface but the shape of the depth distribution profile is not altered. Moreover, in order to obtain the actual depth profiles the samples were not outgassed by heating under a vacuum.

Leakage and capacitance measurements were carried out with AlN films of thickness 2000 ± 100 Å tested with a Talystep comparator. The contact area s between the mercury electrode and the AlN surface was $4.0 \pm 0.2 \times 10^{-3}$ cm^2. Standard high frequency (1 MHz) C–V measurements were performed by using a 72 A Boonton capacitance meter and scanning the electrode bias between -5 and $+5$ V at the frequency of 10^{-1} Hz.

3. RESULTS

3.1. *AES analyses*

Treatments before the analysis of different specimens are given in Table I. The effects of the silicon surface ion etching on the AlN–Si interface composition were studied. The *in situ* ion etching of specimen B for 10 min removed about 200 Å of silicon. About 100 Å of AlN was then deposited simultaneously on specimens A and B. After exposure to the air for 24 h the specimens were analysed together in the ultrahigh vacuum chamber. Auger spectra (Fig. 1) correspond to specimen B at different stages of ion milling. Auger spectra of specimens A and B are similar after a few minutes of ion milling. The AlN Auger spectrum B1 shows a KLL nitrogen peak at 382 eV, a strong peak at 58 eV, a smaller peak at 42 eV and peaks of impurities (a KLL carbon peak at 272 eV, a KLL oxygen peak at 510 eV and an LMM argon peak at 215 eV). The argon atoms had been implanted during ion milling. The $L_{2,3}$ VV Auger transitions of aluminium in Al_2O_3 and in clean metallic aluminium are located at 54 and 67.6 eV respectively[10]. Consequently the peak at 58 eV is assigned to this Auger transition in AlN. The peak at 42 eV could be a satellite peak. The

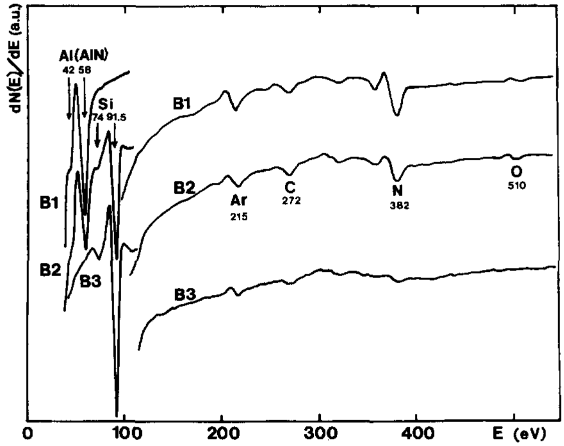


Fig. 1. Typical Auger spectra of AlN film on ion-etched silicon (specimen B): AlN film (B1); AlN–Si interface (B2); silicon substrate (B3).

interface region (25–40 Å thick) is characterized by the simultaneous presence of aluminium, nitrogen and silicon atoms (spectrum B2 in Fig. 1). Nitrogen and aluminium peak amplitudes decrease simultaneously (Fig. 2). The average amplitude of the oxygen Auger peak in specimen A is 2.5 times higher than that in specimen B. No significant difference between the carbon depth profiles was observed for the specimens. Silicon Auger peaks appear at 91.5 and 74 eV with the typical shape for free silicon[11]. When AlN is completely removed, the oxygen content is lower than the AES detection limit (spectrum B3 in Fig. 1).

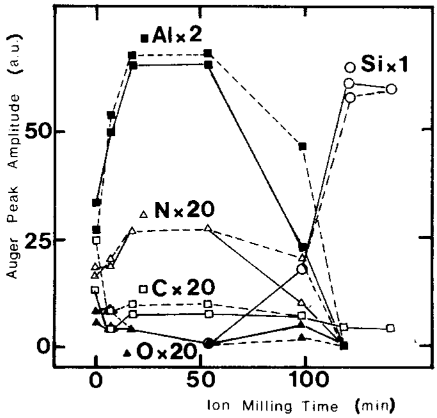


Fig. 2. Aluminium, nitrogen, silicon, oxygen and carbon depth profiles of AlN films on silicon substrates: ——, without treatment (specimen A); – – –, with ion etching before AlN deposition (specimen B). The AlN film thickness was about 100 Å.

The effects of silicon surface chemical treatments were also investigated. The specimens C and D on the one hand and E and F on the other hand were analysed together. Auger spectra of specimen D (Fig. 3) correspond to different stages of ion milling. The Auger peak at 79 eV and its satellite at 64 eV are typical of SiO_2 [12]. The other Auger peaks are assigned to Si LVV (91.5 eV), Ar LMM (215 eV), C KLL (272 eV) and O KLL (510 eV). Plots of the amplitudes of these peaks *versus* the ion milling time are given for specimens C and D in Fig. 4. Silicon (79 eV) and oxygen Auger peaks of specimen C disappear together after milling for about 20 min. For specimen D the silicon (79 eV) peak also disappears after 20 min but it takes 65 min for the oxygen Auger peak to be suppressed. Thus the native SiO_2 layer was nearly the same (10–15 Å average thickness) for the two samples, but oxygen was present at a greater depth when the silicon wafer had been boiled in HNO_3. Specimens E and F were introduced into the ultrahigh vacuum chamber less than 20 min after etching in buffered HF. The main changes in the amplitudes of the Auger peaks occurred during the first 40 min of ion milling (Fig. 5). The carbon Auger peaks are strong, especially for specimen F. The oxygen Auger peak appears only at the end of ion milling. The silicon (79 eV) Auger peak does not appear. In this last case, the native SiO_2 layer removed by chemical etching was not formed again before analysis.

The effects of annealing on the AlN–Si interface composition were studied. The thickness of the AlN film was about 150 Å. After annealing specimen H at 500 °C, specimens G and H were exposed to air for 24 h and then analysed together. The depth profiles of specimens A, B, G and H (Figs. 2 and 6) in AlN film are similar. In the interface region silicon and oxygen atoms are not bonded while aluminium and nitrogen atoms remain chemically bonded. However, the aluminium and nitrogen peak amplitudes for specimens G and H do not decrease simultaneously. Averages of the amplitudes of the oxygen peaks obtained from an analysis of 11 areas in the interface region give 14.8 arbitrary units for specimen G and 8.2 arbitrary units for specimen H.

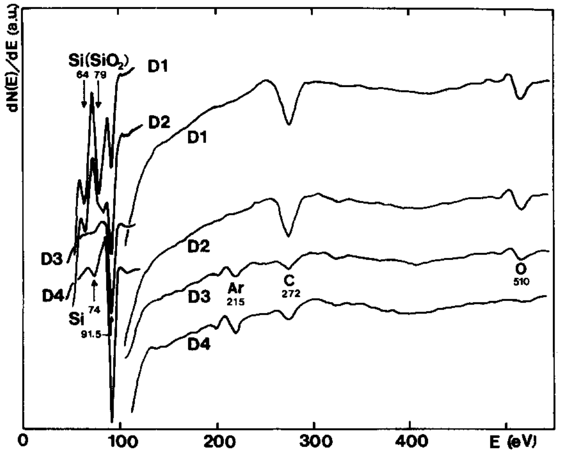
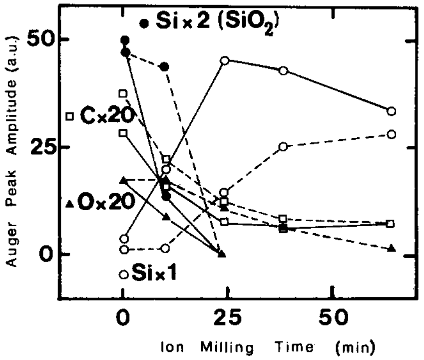


Fig. 3. Typical Auger spectra of silicon substrate boiled in HNO_3 and cleaned (specimen D): before ion milling (D1) and after ion milling for 10 min (D2), 25 min (D3) and 50 min (D4).



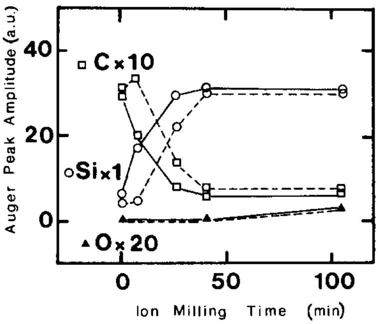


Fig. 4. Silicon in SiO_2 form, free silicon, oxygen and carbon depth profiles of silicon surfaces: ———, cleaned only (specimen C); – – –, boiled in HNO_3 and cleaned (specimen D).

Fig. 5. Silicon, oxygen and carbon depth profiles of silicon surfaces: ——, boiled in HNO_3, etched in buffered HF and cleaned (specimen E); – – –, etched in buffered HF and cleaned only (specimen F).

3.2. Electrical characteristics

The fixed interface charge density N_{AlN-Si} in flat band conditions, the maximum thickness x_d of the depleted area in silicon and the dielectric constant ε_{AlN} of AlN were calculated on the basis of the physical model discussed by Grove[13] and by Sze[14].

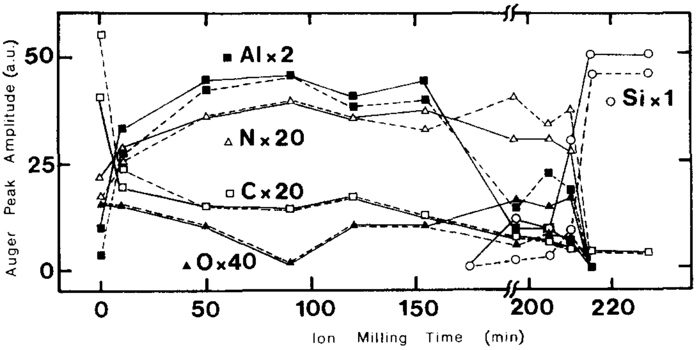


Fig. 6. Aluminium, nitrogen, silicon, oxygen and carbon depth profiles of AlN films on silicon substrates: ———, without treatment (specimen G); - - -, with AlN post-deposition annealing at 500 °C (specimen H). The AlN film thickness was about 150 Å.

TABLE II

LEAKAGE CURRENT AS A FUNCTION OF THE ETCHING TYPE AND THE ANNEALING TEMPERATURE

Silicon surface etching	*Temperature of AlN post-deposition annealing* (°C)	*Leakage current through AlN*[a] (A)	
		Electrode[b] *bias* +5 *V*	*Electrode*[b] *bias* −5 *V*
By Ar$^+$ ion bombardment for a few minutes	Unannealed	10^{-6}	10^{-6}
By Ar$^+$ ion bombardment for more than 10 min	Unannealed	10^{-5}–10^{-4}	10^{-5}–10^{-4}
By buffered HF[c]	Unannealed	(0.5×10^{-5})–10^{-5}	$<10^{-7}$
	>400	$>3\times10^{-5}$	$<10^{-7}$
Unetched	<500	$\approx10^{-6}$	$<10^{-8}$

[a] The AlN film thickness was 2000 ± 100 Å.

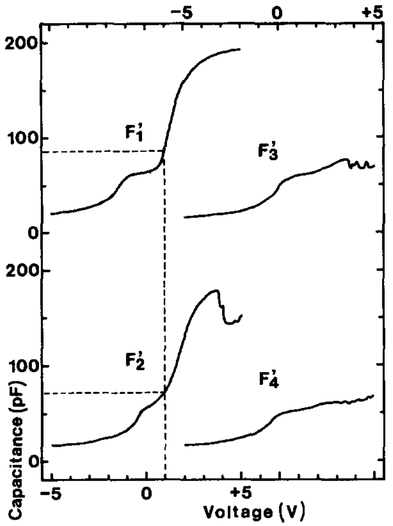
[b] The contact area S between the mercury electrode and the AlN surface was $(4.0\pm0.2)\times10^{-3}$ cm^2.

[c] Etching was followed by cleaning in deionized water.

Leakage currents of the metal–AlN–Si structures are given in Table II. The *in situ* ion etching of silicon involves high ohmic leakage currents through the AlN film. The structure with silicon not etched has lower leakage currents and better thermal stability. C–V plots are given in Figs. 7, 8 and 9. Surface treatment, annealing temperature, flat band voltage and fixed interface charge density are indexed in Table III.

The silicon wafers of specimens F′ are etched and cleaned whereas those of specimens E′ are boiled in HNO_3 before etching (Table III). The behaviours of these two specimens (Figs. 7 and 8) are similar. Plots of C–V characteristics are more complicated than the sigmoid form of the depletion approximation. After annealing above 400 °C the characteristics are greatly impaired (samples F_3', F_4', E_3' and E_4'). The strong leakage currents (Table II) prevent the accumulation of electrons.

The wafers of specimens C′ are only cleaned in deionized water (Table III). The flat band voltage shift between the annealings at 350 and 650 °C is important. The accumulation regime of specimen C′ is only disturbed after annealing at and above 500 °C (Fig. 9). Typical capacitance values are $C_{\min} = 19\pm2$ pF and $C_{\max} = 200\pm4$ pF. Consequently the maximum thickness of the depleted area is $x_d = 1.85\pm0.35$ μm and the dielectric constant of AlN at 1 MHz is $\varepsilon_{\mathrm{AlN}} = 11.3\pm0.5$.



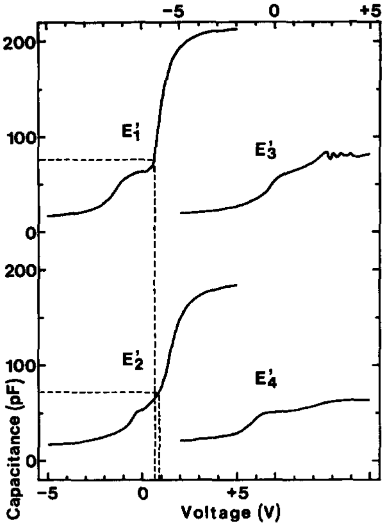


Fig. 7. *C*–*V* characteristics of metal–AlN–Si structures with the silicon surface etched in buffered HF and cleaned (specimen F′): before annealing (F_1') and after annealing at 350 °C (F_2'), 500 °C (F_3') and 650 °C (F_4'). The AlN thickness was about 2000 Å.

Fig. 8. *C*–*V* characteristics of metal–AlN–Si structures with the silicon surface boiled in HNO_3, etched in buffered HF and cleaned (specimens E′): before annealing (E_1') and after annealing at 350 °C (E_2'), 500 °C (E_3') and 650 °C (E_4'). The AlN thickness was about 2000 Å.

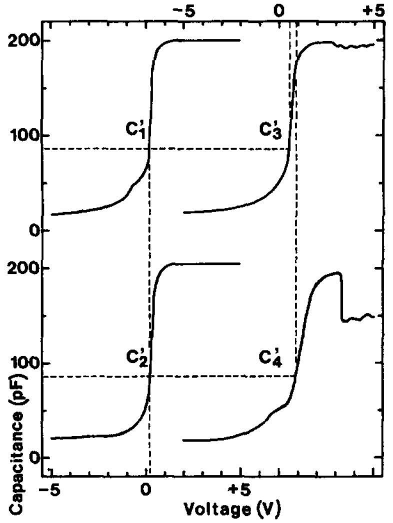


Fig. 9. *C*–*V* characteristics of metal–AlN–Si structures with the silicon surface cleaned only (specimens C′): before annealing (C_1') and after annealing at 350 °C (C_2'), 500 °C (C_3') and 650 °C (C_4'). The AlN thickness was about 2000 Å.

4. DISCUSSION

4.1. Compositions of films, surfaces and AlN–Si interfaces

AES analyses showed that aluminium is always bonded with nitrogen. In

TABLE III

FLAT BAND VOLTAGE V_{FB} AND FIXED INTERFACE CHARGE DENSITY N_{AlN-Si} AS FUNCTIONS OF THE SURFACE TREATMENT AND THE ANNEALING TEMPERATURE

Specimen	*Silicon surface treatment*	*Sample*	*Temperature of AlN post-deposition annealing* (°C)	V_{FB} [a] (V)	N_{AlN-Si} [b] (elementary charges cm^{-2})
F′	Etched in HF and cleaned in H_2O	F_1'	Unannealed	$+1.0 \pm 0.05$	$-(3 \pm 2) \times 10^{10}$
		F_2'	350	$+1.0 \pm 0.05$	$-(3 \pm 2) \times 10^{10}$
E′	Boiled in HNO_3, etched in HF and cleaned in H_2O	E_1'	Unannealed	$+0.65 \pm 0.05$	$+(8 \pm 2) \times 10^{10}$
		E_2'	350	$+0.9 \pm 0.05$	$(0 \pm 2) \times 10^{10}$
C′	Cleaned in H_2O	C_1'	Unannealed	$+0.2 \pm 0.05$	$+(2.2 \pm 0.2) \times 10^{11}$
		C_2'	350	$+0.2 \pm 0.05$	$+(2.2 \pm 0.2) \times 10^{11}$
		C_3'	500	$+0.5 \pm 0.05$	$+(1.2 \pm 0.2) \times 10^{11}$
		C_4'	650	$+0.9 \pm 0.05$	$(0 \pm 2) \times 10^{10}$

[a] For an Hg–AlN–Si capacitive structure with a difference Φ_{MS} in the work functions of the metal and the semiconductor of +0.9 V and for an AlN thickness of 2000 ± 100 Å.

[b] Calculated with $C_{max}/s = 5 \times 10^4$ pF cm^{-2} as constant.

particular, no free aluminium or aluminium oxide (Al_2O_3) was detected. Within the films the oxygen content was roughly zero (Figs. 2 and 6) and this result is consistent with the results of Rutherford backscattering analyses[9].

Oxygen was located at the AlN surface and at the AlN–Si interface within a thickness range of 25–60 Å. The surface oxygen was essentially due to water chemisorbed during the exposure of samples to atmospheric moisture before analysis. The origin of the interface oxygen was the native SiO_2 layer on the silicon surface. AES analysis showed that this oxygen is not chemically bonded to silicon (in SiO_2 or SiO form) or to aluminium (in Al_2O_3 form). The breaking of the O–Si bonds during AlN deposition can occur as the result of an interaction between the SiO_2 layer and the first atomic layers of AlN. The decrease in the interface oxygen content after annealing (Fig. 6) is due to the diffusion of the non-bonded oxygen through the AlN film.

Analysis of silicon surfaces, with or without chemical treatment, always detects large amounts of carbon even if no oxygen is present (Fig. 5). This suggests that the carbon was present in the form of adsorbed hydrocarbon molecules which outgas with difficulty in vacuum at room temperature. The carbon content in bulk silicon was less than 15 atomic ppm[11] and could not be detected by AES. The significant amounts of carbon detected in the depth analysis of the silicon substrate did not originate in the carbon present as an impurity in the bulk silicon. The fast decrease in the amount of carbon during the first period of the ion milling (Figs. 2 and 4–6) is the result of high sputtering yields of surface hydrocarbons. Simultaneously, the argon ion bombardment cracked hydrocarbon molecules, resulting in the appearance of residual carbon atoms. During ion milling the amount of residual carbon decreased slowly because of the low sputtering yield of carbon atoms.

4.2. *Electrical properties of metal–AlN–Si structures*

The nucleation and growth process of the film and its subsequent structural defect density are affected by the state of the substrate surface. It is known that ion bombardment disturbs the surfaces of solids. In the present case the strong leakage currents through AlN film deposited on ion-etched silicon are likely to be the result of a high density of structural defects. The dielectric constant of AlN is consistent with the value 11.5 ± 0.2 obtained by Chu and Kelm[1] for AlN deposited by pyrolysis of the adduct compound $AlCl_3 \cdot NH_3$ between 800 and 1000 °C. The theoretical thickness of the depleted area under a strong inversion regime, calculated by means of the depletion approximation, is 1.0 ± 0.1 μm [13], whereas the value deduced from C–V measurements is 1.85 ± 0.35 μm. Steps on C–V curves correspond to a weak inversion beginning near the silicon surface. However, the leakage currents produced by increasing negative bias oppose the formation of a p-type inversion layer because of electron injection through the AlN film near the silicon surface. The consequent sharp drop in capacitance corresponds to a deep depletion regime without inversion. Moreover, the lack of flat band voltage hysteresis confirms that the leakage currents prevent an eventual charge storage[3].

The fixed charges (Table III) are positive for specimens C′, with the native SiO_2 layer of the silicon substrate not removed before AlN deposition. Above 350 °C the density of these positive fixed charges, induced by the oxygen in the interface, decreases with increasing annealing temperature. The chemical etching of the silicon substrate (specimens F′) induces negative fixed charges at the interface. These interface charges remain stable during annealing up to 350 °C (no flat band voltage shift). The characteristics of the specimens E′ are located between the characteristics of the specimens F′ and C′ (Figs. 7–9).

5. SUMMARIZING REMARKS AND CONCLUSIONS

Ion- and chemical-etching effects on the chemical composition of the silicon surface and AlN–Si interface were studied. AlN films were deposited at room temperature by reactive sputtering. C–V characteristics of the metal–AlN–Si structures were investigated on some specimens before and after annealing. The experimental methods, results and correlations between chemical composition and electrical properties were discussed.

The composition of the different AlN–Si interfaces changed markedly in a thickness of 25–40 Å. Chemically bonded aluminium and nitrogen, free silicon, and oxygen as an impurity were present simultaneously. Interface oxygen originated from the native SiO_2 layer dissociated during AlN deposition. Residual surface carbon was the result of initial surface contamination by hydrocarbons.

The electrical characteristics of the metal–AlN–Si structure were better when the native SiO_2 layer on the silicon substrate had not been removed before AlN sputtering. However, non-ohmic leakage currents through the AlN film prevented the formation of an inversion layer. The density of positive fixed charges induced by the interface oxygen was about $(2\text{–}2.5) \times 10^{11}$ cm^{-2}. On annealing at 650 °C the interface oxygen diffused through the AlN film and the fixed charge density was reduced to $\pm 2 \times 10^{10}$ cm^{-2}. With AlN films sputtered onto chemically etched silicon the interface charge densities were less than $+2 \times 10^{10}$ cm^{-2} without annealing. These values correspond to a typical AlN–Si interface not contaminated by oxygen and are better than the values of about 10^{11} cm^{-2} for a typical SiO_2–Si interface resulting from the thermal oxidation of silicon[15].

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