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https://doi.org/10.15017/16683

出版情報：九州大学大学院総合理工学報告. 25 (1), pp.1-6, 2003-06. 九州大学大学院総合理工学府
バージョン：
権利関係：

九州大学大学院総合理工学報告
第25巻 第1号 1-6頁 平成15年6月

Engineering Sciences Reports, Kyushu University
(KYUSHU DAIGAKU SOGORIKOGAKU HOKOKU)
Vol. 25, No. 1 pp. 1-6 JUNE. 2003

Silicon Dioxide Film Deposition by Afterglow-Plasma-Enhanced Chemical Vapor Deposition using Triethoxysilane and Tetraethoxysilane

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(Received March 31, 2003)

Silicon dioxide (SiO_2) films were deposited by afterglow-plasma-enhanced CVD using triethoxysilane (TRIES) and tetraethoxysilane (TEOS) as source materials. TRIES has approximately four times higher vapor pressure than TEOS. The growth rate using TRIES was approximately twice as high as that using TEOS under the same operating conditions. The step coverage of film grown by TRIES was better than that by TEOS under a wide range of operating conditions. These results suggest that TRIES is a good candidate for SiO_2 films.

Key words: *CVD, SiO_2, Afterglow plasma, Triethoxysilane, Tetraethoxysilane*

1. Introduction

Silicon integrated circuit (IC) technology is being rapidly developed, which requires shrinkage of device dimensions and increase in device package density[1]. The manufacturing processes of IC must be operated at relatively low temperatures to prevent the excessive diffusion of dopant and damage to the metal line. To realize low temperature processes, many thin film growth processes for IC manufacture are assisted by plasma. In general, if the substrates are exposed directly to the plasma, the devices manufactured on the substrates become damaged by factors such as plasma because of charging and ion bombardment[2), 3)]. The afterglow-plasma-enhanced CVD (AG-PECVD) can reduce these plasma damages. The apparatus of the AG-PECVD is separated into two zones; one is the zone for activating sources by plasma discharge and the other is the zone for film grown on the heated substrate. The ions rapidly recombine outside of the plasma zone, but long-lived and metastable radicals or intermediates are transported downstream to the substrate surface and form films[4)-6)]. Thus, AG-PECVD is expected to have the advantages of both thermal CVD and PECVD.

Silicon dioxide (SiO_2) films are one of the most important materials used for interlayer dielectrics and are indispensable for the LSI industry[1), 7)]. In recent years, SiO_2 films have been widely studied using methods such as thermal CVD[8)], laser ablation[9)], electron cyclotron resonance (ECR) PECVD[10), 11)], photo-assisted CVD[12)-14)], and the sol-gel method[15), 16)].

Among the source materials for SiO_2 film growth, tetraethoxysilane [$Si(OC_2H_5)_4$, TEOS] has been widely used in the semiconductor industry because of its excellent gap-filling ability and low deposition temperature.

In a triethoxysilane [$HSi(OC_2H_5)_3$, TRIES], which has less ethoxy ($-OC_2H_5$) substrate, even four times higher vapor pressure than TEOS, high growth rate can be expected without a heating source material. However, there are only a few papers on the characteristics of SiO_2 CVD using TRIES being reported. In this work, the characteristic of SiO_2 CVD using TRIES/TEOS in horizontal hot-wall AG-PECVD, such as morphology, growth rate and step coverage under various operating conditions were studied. Also, we attempted to find out the role of the plasma by using two types of reactors, that is, straight and branch-type tubular reactors.

2. Experiment

Figure 1 shows the schematic diagram of the AG-PECVD reactor. The vapor of TRIES and TEOS being heated at 303-333K and at 333K, respectively, was carried by nitrogen (N_2) gas. The gas lines were heated over 15K higher than the evaporator temperature to prevent condensation of the vapor. We have investigated the role of the plasma process using three kinds of gas feed method in two types of reactors. First, TRIES / N_2 / Oxygen (O_2) gas was passed through the electrodes and was activated by the plasma in the straight reactor as shown in Fig.1b. Second, O_2 / N_2 gas was injected into the plasma zone and TRIES / N_2 gas was fed into the growth zone without passing through the electrodes (Fig.1c). Third, the gas lines of O_2 / N_2 and TRIES / N_2 were alternated for the second method. However, in the

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third method, the films were grown at over 873K, almost similar to the TRIES / O_2 LPCVD experiment previously reported[17], because the ozone and activated oxygen cannot be produced. Thus, we detail the experiments using the first and second methods.

Films were deposited on silicon p-type wafers on which a trench pattern was etched and on the inner surface of short quartz tubes in the reactor. We cleaned the substrate with acetone and purified the water to remove organic impurities.

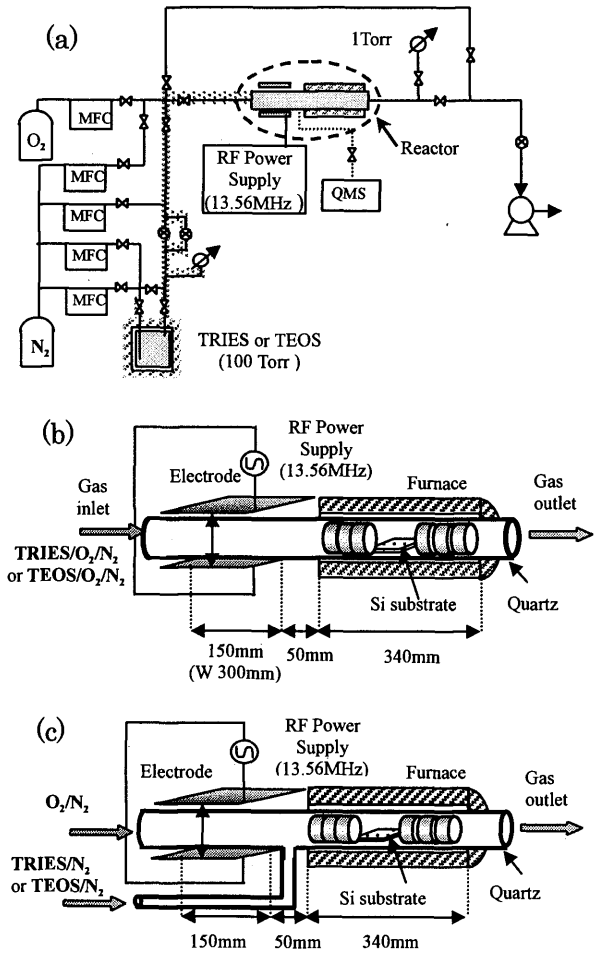

Fig.1 Schematic diagram of the AG-PECVD reactor

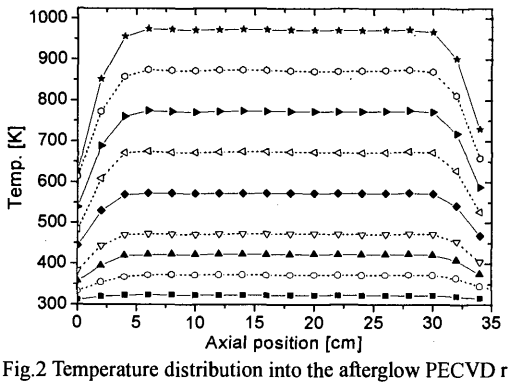

Fig.2 Temperature distribution into the afterglow PECVD reactor

The electrodes consisted of two parallel plates (L150mm × W300mm) made of aluminum and the distance between the two electrodes was 25mm, with a rf power of 13.56MHz. The distance between the electrodes and the furnace (L340mm × ID20mm) was 50mm. The uniform temperature distribution of the reactor was realized over 26cm (from 4cm to 30cm from the reactor inlet)(Fig.2, at 323K– 973K). The film growth rate was determined by the weight change before and after the growth experiments. The morphology and step coverage was observed by scanning electron microscopy (SEM). The composition in the gas phase was analyzed using a quadrupole mass spectrometer (QMS). Experimental conditions are summarized in Table I and each experiment was classified in Table II. In case 1, the TRIES / N_2 / O_2 gas was passed through the electrodes and activated by plasma in the straight tubular reactor as shown in Fig.1b. In case 2, the O_2 / N_2 gas was supplied into the plasma zone and the TRIES / N_2 gas was supplied into the film growth zone without passing through the electrodes (Fig.1c). Case 3 and 4 were alternated with TRIES and TEOS.

Table I Experimental conditions

· Substrate Temp.	:	323~873 K
· RF Power	:	0~150 W
· O_2 Conc.	:	0~50 mol%
· TRIES Conc.	:	0~10 mol%
· Pressure	:	133 Pa (1Torr)
· Time	:	30~120 min
· Total Flow Rate	:	200 sccm
· Carrier Gas	:	N_2

Table II Classification of each experiment

	Experiment.
Case 1	TRIES/O_2/N_2 plasma
Case 2	O_2/N_2 Plasma + TRIES/N_2
Case 3	TEOS/O_2/N_2 plasma
Case 4	O_2/N_2 plasma + TEOS/N_2

3. Results and Discussion

3.1 Effects of rf power and GR distribution

Figure 3 shows the average growth rate under different rf powers at 673K. The growth rates in cases 2 and 4 were approximately twice as high as those in cases 1 and 3, and the growth rate from TRIES was approximately twice as high as TEOS. M. Adachi *et al.* estimated the ozone concentration (C_{O3}) with distance from the reactor inlet[18]. They showed that the C_{O3} decreased rapidly along the flow direction. T. Kawahara *et al.*[19] and C. S. Pai *et al.*[20] showed that ozone and activated oxygen play an important role in SiO_2 film growth using TEOS.

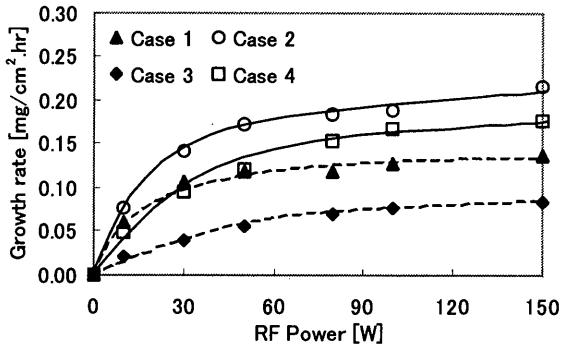

Fig.3 Growth rate vs. rf power when deposited at 673K, 1.27mol% TRIES / TEOS and 50mol% O_2.

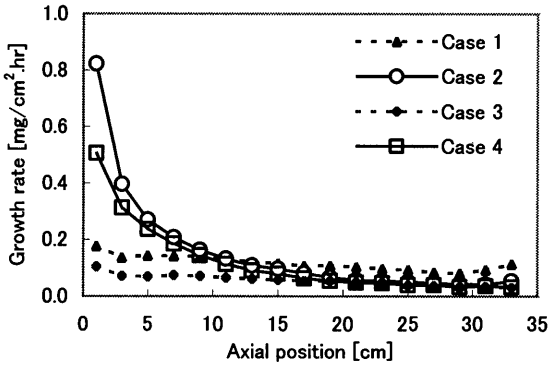

Fig.4 Growth rate distributions along the flow direction at 673K, rf 50W, 1.27mol% TRIES / TEOS and 50mol% O_2.

In cases 1 and 3, most of the ozone and activated oxygen that were formed in the plasma zone reacted with the source and/or intermediates and formed oligomers or polymers (hereafter, "polymer" represents oligomer and polymer) of TRIES / TEOS as intermediates in the plasma zone. The amount of polymers increased with rf power and formed an SiO_2 film from the plasma zone to the afterglow zone. In fact, many SiO_2 particles became deposited on the wall of the plasma zone. On the other hand, in cases 2 and 4, the ozone and activated oxygen which had been synthesized in the plasma zone began to react with TRIES / TEOS to form polymers after the mixing zone. White-colored SiO_2 particles were observed after the mixing zone. The particle quantity from TRIES was larger than that from TEOS. In all cases, the growth rate of the film increased with rf power. The growth rate distributions on the substrate in cases 1 and 3 were very uniform, however, in cases 2 and 4, large peaks were observed near the reactor inlet and decreased exponentially along the flow direction (Fig.4). The concentrations of ozone and activated oxygen ($C_{O3/O*}$) and the concentrations of TRIES / TEOS ($C_{TRIES/TEOS}$) in the growth zone in cases 1 and 3 were considerably low, because both began to react in the plasma zone and formed SiO_2 powders in the plasma zone up to the inlet of the film growth zone. On the contrary, $C_{O3/O*}$ and $C_{TRIES/TEOS}$ at the reactor inlet in cases 2 and 4 were comparatively high because of no reaction between them in the plasma zone.

3.2 Effects of deposition temperature

As shown in Fig.5, the growth rate in case 1 was proportional to temperature, however, that in case 2 was inversely proportional to temperature. In case 1, the films could not deposit at low temperatures below 423K, while in case 2 they deposited at even 323K.

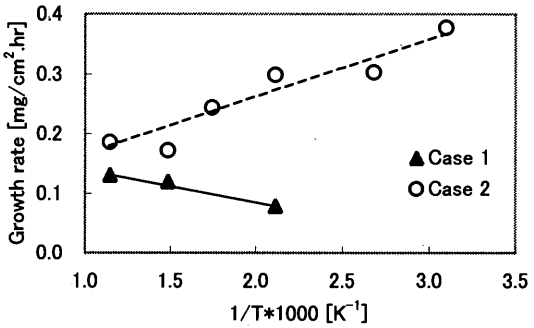

Fig.5 Growth rate on temperatures when deposited with rf 50W, 1.27mol% TRIES.

Table Ⅲ Annealing results at 873K for 3 hrs.

Temp.[K]	TRIES		TEOS	
	Case1	Case2	Case3	Case4
473	-31.4%	-11.8%	-60.2%	-35.3%
673	-7.2%	-5.2%	-10.9%	-14.4%

Table Ⅲ shows the weight change of the film before and after annealing at 873K for 3 hrs. The weight changes of films grown at 473K in cases 1 and 3 are larger than those in cases 2 and 4, thus the films grown using TRIES / TEOS in cases 1 and 3 contains more organic impurities than those in cases 2 and 4, because the temperature is too low to oxidize completely. On the other hand, at high temperatures (673K), it is sufficient to oxidize for preparing SiO_2 film, so the weight changes are small in all cases. The films in cases 2 and 4 contains less organics than those in cases 1 and 3 as shown in Table Ⅲ. In cases 1 and 3, TRIES / TEOS reacts with the ozone and active oxygen and polymerizes in the plasma zone. The heavy polymers partially oxidized flow into the growth zone and form the SiO_2 film, however, it is difficult for heavy polymers to be oxidized with low $C_{O3/O*}$, so the film in cases 1 and 3 contains a lot of organic impurities. On the other hand, in cases 2 and 4, TRIES / TEOS reacts with high $C_{O3/O*}$ from the mixing zone and formed SiO_2 film with few organic impurities.

3.3 Effects of TRIES concentration (C_{TRIES}) and O_2 concentration

Effects of C_{TRIES} on the growth rate are shown in Fig. 6 (O_2: 50mol%, N_2: balanced). The growth rate in case 1 rapidly increased linearly to 1.27mol% TRIES and then gradually increased with C_{TRIES}. On the other hand, the growth rate in case 2 rapidly increased up to 0.6mol% TRIES, and then it gradually decreased. Figure 7 shows the growth rate under various concentrations of oxygen.

The growth rate in case 1 rapidly increased up to 15mol% O_2, and then it gradually increased. In case 2, over 20mol% O_2 it was saturated.

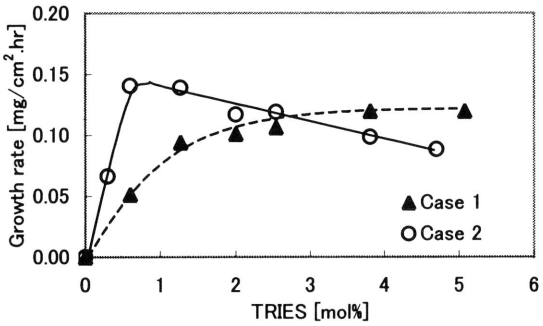

Fig.6 Growth rate on C_{TRIES} when deposited at 673K with 50mol% O_2 and rf 50W.

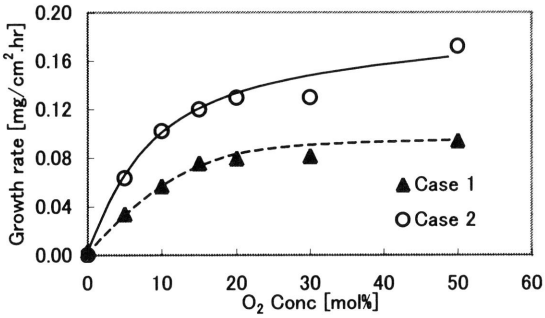

Fig.7 Growth rate vs. O_2 concentration when deposited at 673K and rf 50W.

3.4 Step coverage

The film using TEOS grows thick at the bottom and thin at the top in microscale trenches like a liquid. This coverage profile is called a "flow-like shape" [21), 22)]. The flow-like shape is very useful for depositing the SiO_2 film as an insulator or a dielectric on the rough surface in the process of IC chips fabrication. However, the flow-like shape using TEOS has not been found at PECVD because that might be caused by an excess polymerization in the gas phase, and the flow-like shape was formed by monomer or dimer of TEOS[23)-25)]. The step coverage in case 1 was poor regardless of growth position (Figs.8a and 8b). The poor step coverage causes defective insulation[21)]. The step coverage in case 2 was dependent on the substrate position and the $C_{O3/O*}$. The film grown at 10cm has a better step coverage (Fig.8d), however there is no flow-like shape in any operating conditions via TRIES by AG-PECVD.

3.5 Discussion of film growth using TRIES

The molecular structure of TRIES is like that of TEOS as shown in Fig.9. The distribution of the growth rate in the reactor (in the plasma zone and in the growth zone) and on a microscale roughness (step coverage) using TRIES is also similar that using TEOS. The reaction mechanism for preparing SiO_2 film using TRIES must be similar to that using TEOS as M.Adachi et al report[24), 25)].

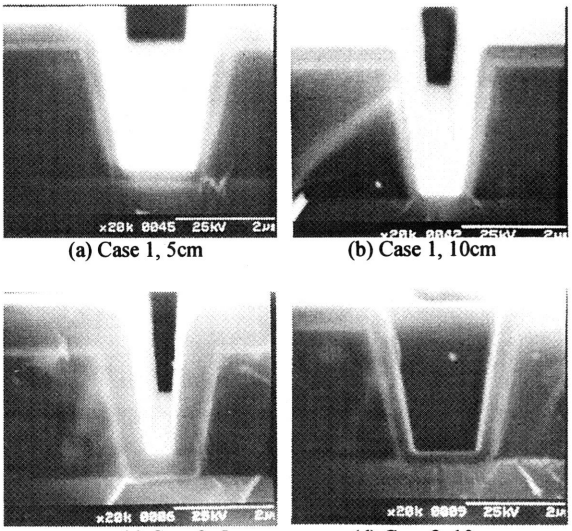

Fig.8 SEM photographs at 673K and rf 50W

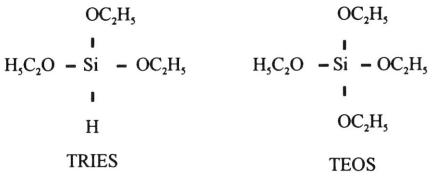

Fig.9 Molecular structure of TRIES and TEOS

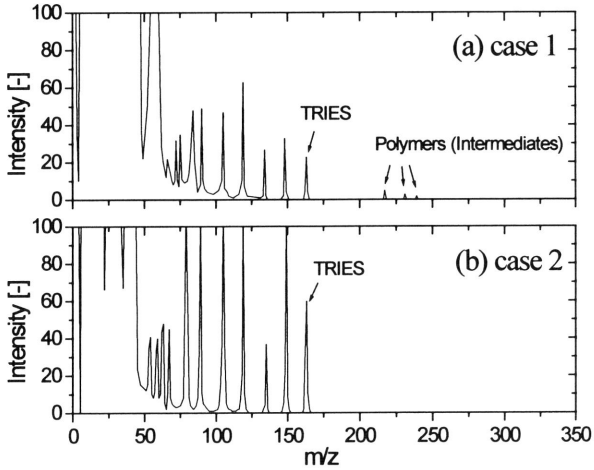

Fig.10 Mass spectra in the rear of the plasma zone at room temperature

In case 1, the TRIES and O_2 are both introduced into the plasma zone, so that heavy polymers of TRIES are formed and flow into the growth zone. The heavy polymers are difficult to oxidize, so the SiO_2 film contains a large amount of organic impurities. In case 2, the ozone and active oxygen are produced in the plasma zone and mixed with TRIES after the mixing zone. The TRIES forms the SiO_2 film containing few organic impurities with sufficient oxidization by ozone and active oxygen with partially polymerizing of TRIES in the gas phase. Figure 10 shows the mass spectra just

after the plasma zone at room temperature. The polymers of TRIES (m/z:164.3) are detected in case 1 as shown in Fig.10a. This is evidence of the polymerization reaction of TRIES in the plasma zone. The polymerization also occurs by plasma without ozone or activated oxygen.

4. Conclusions

The SiO_2 films were deposited by afterglow-plasma-enhanced CVD (AG-PECVD) using triethoxysilane (TRIES) and tetraethoxysilane (TEOS) as source materials. We mainly executed two kinds of experiment for investigation of the plasma process as follows. First, when all gases, TRIES / O_2 / N_2, were supplied into the front of the plasma zone, the films were grown at over 423K and the growth rate was proportional to the temperature. Second, when O_2 / N_2 was supplied into the plasma zone and TRIES / N_2 was supplied into the front of the growth zone, the films were deposited at even 323K and the growth rate had large peaks near the inlet of the growth zone and rapidly decreased along the flow direction. This may be attributed to the difference of the concentration of the ozone and activated oxygen (C_{O3/O^*}) at the reactor inlet. In other words, the ozone and activated oxygen were produced in plasma with a straight tube reactor and they reacted with monomers or intermediates in the plasma zone, so that the C_{O3/O^*} at the reactor inlet was low. However, the ozone and activated oxygen in the branch tube reactor started to react with monomers in the mixing zone, so that C_{O3/O^*} was relatively high. As a result, the C_{O3/O^*} resulted in a difference of initial deposition temperatures for each experiment. In other words, the deposition was strongly dependent on the C_{O3/O^*}. A poor-quality film at low temperature was caused by insufficient surface reaction, while a high quality film at high temperature was caused by sufficient surface reaction of C_2H_4 and H_2O elimination reaction. Thus, a relatively high temperature is necessary for preparing a high-quality SiO_2 film. Overall, the films from TRIES were superior to those from TEOS. This indicates that TRIES can be a good candidate for SiO_2 film deposition.

Acknowledgement

The authors thank Mr. Ichise for his support in this work.

References

1) C.S.Pai and C.P.Chang, J. Appl. Phys., 68(2), 793 (1990).
2) E.van der Drift, R.Cheung and T.Zijlstra, Microelectron. Eng., 32, 241 (1996).
3) B.Y.Tsui, S.S.Lin, C.S.Tsai and C.C.Hsia, Microelectron. Rel., 40, 2039 (2000).
4) C.Bayer, E.Bapin and Ph.Rudolf von Rohr, Surf. Coat. Technol., 116-119, 874 (1999).
5) J.L.Vossen and W.Kern, "Thin film process II", Academic press (1991) p.37.
6) A.M.Wrobel, S.Wickramanayaka and Y.Hatanaka, J. Appl. Phys., 76(1), 558 (1994).
7) T. Homma, Mater. Chem. Phys., 41, 234 (1995).
8) J.J.Senkevich and S.B.Desu, Chem. Vap. Dep., 4(3), 92 (1998).
9) M.Okoshi, M.Kuramatsu and N.Inoue, Jpn. J. Appl. Phys., 40, L41 (2001).
10) K.Sano, S.Hayashi, S.Wickramanayaka and Y.Hatanaka, Thin Solid Films, 281-282, 397 (1996).
11) P.Bulkin, N.Bertrand and B.Drevillon, Thin Solid Films, 296, 66 (1997).
12) N.Suzuki, K.Masu, K.Tsubouchi and N.Mikoshiba, Jpn. J. Appl. Phys., 29(12), 2341 (1990).
13) N.Suzuki, K.Masu and K.Tsubouchi, Appl. Surf. Sci., 79-80, 327 (1994).
14) K.Kurosawa, N.Takezoe, H.Yanagida, J.Miyano, Y.Motoyama, K.Toshikawa, Y.Kawasaki and A. Yokotani, Appl. Surf. Sci., 168, 37 (2000).
15) M.H.Jo, J.K.Hong, H.H.Park, J.J.Kim, S.H.Hyun and S.Y.Choi, Thin Solid Films, 308-309, 490 (1997).
16) N.Primeau, C.Vautey and M.Langlet, Thin Solid Films, 310, 47 (1997).
17) B.H.Kim, R.Okazaki, Y.Akiyama, T.Sato and N.Imaishi, 九州大学機能物質科学研究所報告, 11(2), 99 (1997).
18) M.Adachi, K.Okuyama, T.Fujimoto, J.Sato and M.Muroyama, Jpn. J. Appl. Phys., 35, 4438 (1996).
19) T.Kawahara, A.Yuuki and Y.Matsui, Jpn. J. Appl. Phys., 31, 2925 (1992).
20) C.S.Pai, J.F.Miner and P.D.Foo, J. Appl. Phys., 73(7), 3531 (1993).
21) C.Y.Chang and S.M.Sze, "ULSI Technology", McGraw-Hill (1996), p.414.
22) K.Fujino, Y.Nishimoto, N.Tokumasu and K.Maeda, J. Electrochem. Soc., 137(9), 2883 (1990).
23) Z.Yuan, S.Mokhtari, A.Ferdinand, J.Eakin and L.Bartholomew, Thin Solid Films, 290-291, 422 (1996).
24) M.Adachi, K.Okuyama, N.Tohge, M.Shimada, J.Sato and M.Muroyama, Jpn. J. Appl. Phys., 31, L1439 (1992).
25) M.Adachi, K.Okuyama, N.Tohge, M.Shimada, J.Sato and M.Muroyama, Jpn. J. Appl. Phys., 33, L447 (1994).