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Epitaxial Growth of Aluminum Nitride Thin Films on (111)Si by ECR Dual Ion Beam Sputtering.

H. Okano, N. Tanaka, Y. Kobayashi, T. Usuki and K. Shibata
New Materials Research Center, SANYO Electric Co., Ltd.
1-18-13, Hashiridani, Hirakata, Osaka, Japan

AlN thin films have been epitaxially grown on a (111)Si substrate by ECR dual ion beam sputte The effects of the initial growth process on film properties, such as crystal orientation and crystallinity, investigated by RHEED patterns and AFM images. A single crystal AlN film with a (001) plane parallel t substrate was obtained on (111)Si at a substrate temperature of more than 600°C by growing a half at layer of aluminum before the deposition process. A half atomic layer of aluminum on (111)Si was enoug prepare the single crystal AlN film. C-axis oriented AlN thin film was obtained on (111)Si with su nitriding at a substrate temperature of more than 300°C.

1. Introduction

Aluminum nitride (AlN) thin films grown on silicon substrates are very promising materials for GHz-band bulk and surface acoustic wave (SAW) devices because of their high acoustic velocity and piezoelectricity, also their passivation and insulating properties [1-3]. Epitaxial growth techniques for AlN films with high crystallinity and a smooth surface are very important for these applications. There have been many reports on the epitaxial growth of AlN films on silicon substrates by chemical vapor deposition (CVD) [4,5] and molecular beam epitaxy (MBE) [6]. In these reports, the growth conditions, such as the pretreatment of the substrate surface, growth temperature, growth rate and the kind of gas source, have a great influence on crystallinity, crystal orientation and surface morphology. We have been considering that controlling the initial growth process is very important to the preparation of high-quality AlN film.

In this paper, AlN films are prepared on (111)Si by electron cyclotron resonance (ECR) dual ion beam sputtering methods which can separately control the aluminum flux rate and nitrogen ion beam energy. The effects of the initial growth process, such as surface nitriding and aluminum metallization, on film properties were investigated by RHEED patterns and AFM image.

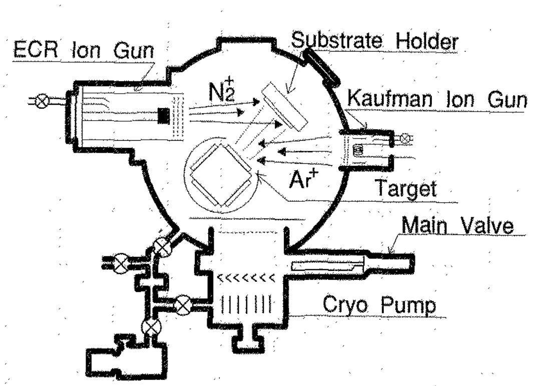


Fig.1 ECR dual ion beam sputtering system.

2. Experiments

The ECR dual ion beam sputtering met used to grow AlN films. Figure 1 shows the a for this system. Table I shows the best d conditions for preparing single crystal AlN sapphire substrates [7]. The (111)Si substrate wa by thermal annealing at 800°C for about 1 h vacuum of less than 2×10^{-7} Torr. The natural S can be almost completely removed by this treat carbon contamination remains on the surface be removal of carbon is more difficult than that of The control method for the initial growth pro pretreatment before the growth process, is descri

Table I Deposition conditions

Target	Aluminum
Substrate temperature	300-800°C
Nitrogen gas flow rate	8 CCM
Argon gas flow rate	4 CCM
Nitrogen ion beam	100 eV, 0.32 mA/
ECR microwave power	300 W
Argon ion beam	800 eV, 0.7 mA/
Final pressure	less than 2×10^{-7}
Deposition pressure	7.0×10^{-5} To

In this experiment, two types of pretreatm examined. One is substrate nitriding by a nitr beam using an ECR ion source before the d process and the other is the aluminum metalliz few layers on (111)Si substrates. Surface nitri carried out by irradiating nitrogen ion beams energy of 100 eV and current density of 0.32 m an ECR ion source. Aluminum was deposite beam sputtering at a flux rate of 0.5Å/s. The a of aluminum was carried out onto a (111)Si heated to a desired temperature from 300°C to 80 aluminum coverage on the (111)Si substrate is % at the deposition time of 6 sec.

Reflection high-energy electron di (RHEED) and x-ray diffraction (XRD) were investigate the crystallinity, crystal orientation and epitaxial relationship. An atomic force microscope (AFM) was used to examine the surface morphology.

3. Results and discussions

3.1. Growth of AlN films on (111)Si with surface nitriding

AlN films were deposited on (111)Si with surface nitriding at the growth temperature of 300-800°C and film thickness of 1000Å. Table Ⅱ shows crystal properties estimated by RHEED pattern. C-axis oriented AlN film and poly-crystalline film were obtained on (111)Si with surface nitriding at a growth temperature of 500°C-800°C and 300°C-400°C, respectively. Single crystal AlN can not be obtained because of the existence of a non-crystal silicon nitride (SiN) phase on (111)Si. Figure 2 shows the RHEED pattern of AlN film grown on (111)Si with surface nitriding at growth temperature of 800°C. This RHEED pattern appeared when the sample was rotated around the c-axis of AlN at an interval of 30 degrees. This result is the same as that of CVD methods reported by Chubachi et al [4]. The AlN film grown on (111)Si with surface nitriding consists of two types of epitaxial growth with a differential direction in the a-axis. In this paper, this film is called c-axis oriented film.

Table Ⅱ The crystal properties of AlN films on the (111)Si with surface nitriding at the various growth temperature. The propertiy was estimated by RHEED patterns. The open circles and open triangle indicate c-axis oriented and poly-crystalline phase, respectively,

Ts(°C)	300	400	500	600	700	800
phases	△	△	○	○	○	○

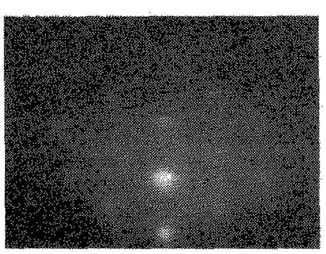
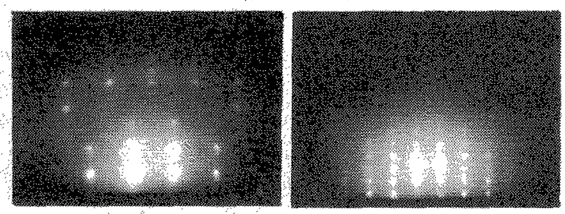


Fig.2 RHEED pattern of AlN film grown on (111)Si with surface nitriding.

Next, AlN film with a thickness of about 30Å was estimated by RHEED in order to determine the initial growth process in detail. The RHEED pattern of AlN film with thickness of 30Å have a hollow pattern. These RHEED patterns indicate that AlN film grown on (111)Si with surface nitriding is non-crystal. The RHEED patterns of AlN with a thickness of 200Å have a ring pattern. These results suggest that the crystal properties of AlN films grown on (111)Si with surface nitriding change from non-crystal to poly-crystal and from poly-crystal to c-axis oriented with increases in film thickness. We thought that this change of crystal properties would have an influence on the growth temperature and growth rate. However, we can not investigate this phenomenon in detail in this paper.



(a) (b)

Fig.3 RHEED patterns of AlN films grown on (111)Si with a 0.5 atomic layer of aluminum. (a) :electron beam incident to the [110] direction of (111)Si,(b): electron beam incident to the [110] direction of (111)Si.

3.2. Growth of AlN films on (111)Si with Al metallization

(a) Effects of Al layer on (111)Si

Effect of aluminum metallization on (111)Si before the deposition process, which affects the initial growth process, was investigated to determine the influence on film properties, such as crystallinity, uniformity and orientation. AlN film was deposited on (111)Si with a 0.5 atomic layer of aluminum under the growth temperature of 800°C. It was confirmed from XRD patterns that (001) plane of hexagonal AlN is parallel to the (111)Si. Figure 3 shows the RHEED pattern of AlN film grown on (111)Si with a 0.5 atomic layer of aluminum. The film thickness was 1000Å. Figure 3-(a) shows the case of an electron beam incident to the [110] direction of (111)Si. This RHEED pattern conforms to the theoretical pattern of an electron beam incident to the [110] direction of hexagonal AlN. On the other hand, Fig.3-(b) shows the case of an electron beam incident to the [1$\bar{1}$0] direction of (111)Si. This RHEED pattern conforms to the theoretical pattern of an electron beam incident to the [1$\bar{1}$0] direction of hexagonal AlN. These results indicate that a (001) plane of AlN is epitaxically grown on (111)Si. But it seems that the epitaxial growth mode is not layer by layer, i.e., is three-dimensional growth, because RHEED patterns were spotty. The epitaxial relationship is as follows:

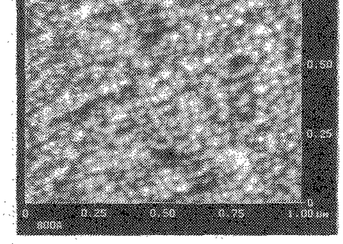


Fig.4 AFM images of AlN films grown on (111)Si with a 0.5 atomic layer of aluminum.

(001)AlN//(111)Si, [110]AlN//[110]Si.

This relationship is the same as that in previous reports [4]. Figure 4 shows AFM images of this AlN films grown on (111)Si with a 0.5 atomic layer of aluminum. It was found from the AFM images that the surface roughness of this AlN film with a 0.5 atomic layer of aluminum was smoother than that of the AlN film grown by CVD methods [4]. It was confirmed from these results that a 0.5 atomic layer of aluminum on (111)Si was enough to prepare single crystal AlN film. It was considered that epitaxial AlN film could be obtained by using a (111)Si substrate with an aluminum layer because the growth of a non-crystalline-SiN phase was disturbed by the aluminum layer. In general, single crystal AlN with smooth surface can not be obtained using (111)Si because non-crystalline SiN is grown on (111)Si by introducing nitrogen gas before the growth process. Recently, it has been well known from scanning tunnelling microscopy (STM) studies that a clean surface of (111)Si reconstructs to (111)Si 7×7 structure at a surface temperature of more than 600°C in ultra high vacuum. Aluminum forms several ordered surface phases on the (111)Si 7×7 structure depending on the substrate temperature and aluminum coverage [9-11]. One of the several ordered surface phase is the γ-phase. The aluminum atom of this phase is adsorbed by the dangling bond of the silicon atom. However, there is a lack of consensus even about the periodicity of this phase. Very recently, K.Nishiyama et al. have reported that γ-phase of aluminum has a strong influence on the epitaxial growth of (001)AlN on (111)Si with an aluminum layer [12]. Unfortunately, they do not discuss the mechanism of this epitaxy in detail.

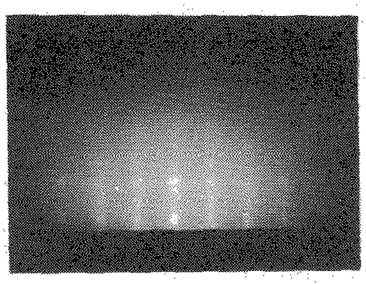


Fig.5 RHEED pattern of AlN films grown on (111)Si with a 0.5 atomic layer of aluminum at the growth temperature of 800°C and film thickness of 30Å.

Next, AlN film with a thickness of about 30Å was estimated by RHEED in order to determine the initial growth process in detail. Figure 5 shows the RHEED pattern of the AlN film grown on (111)Si with a 0.5 atomic layer of aluminum at the growth temperature of 800°C. The RHEED patterns shown in Fig.5 are more streaky than that of AlN having a film thickness of 1000 Å(Fig. 3-(a)). This RHEED has almost a spotty pattern. If the electron beam incidence is rotated around the c-axis of the AlN, two types of RHEED patterns appear at interval of 30 degrees. It was found from this result that single crystal AlN with a thickness of only 30Å can be obtained, but three-dimensional growth, i.e., islan growth, already occurred at the initial growth proces K.Nishiyama et al. reported that (001)AlN can b epitaxially grown on (111)Si with a 0.6 atomic layer c aluminum by MBE, and that the RHEED pattern of th AlN film with a thickness of less than 300Å is ver streaky, with the AlN grown layer by layer [12]. It seem that the difference in these results is due to the growt conditions, such as the aluminum flux rate an background pressure before the growth process.

Table Ⅲ The crystal properties of AlN films on (111)Si with a 0.5 atomic layer of Al at the various growth temperature. Al layers were grown at the same temperature as that of preparing AlN. The twofold circles, open circles and open triangle indicate single crystalline, c-axis oriented and poly-crystalline phase, respectively,

Ts(°C)	300	400	500	600	700	800
phases	△	△	△	○	◎	◎

(b) Dependence of growth temperature

We investigated the dependence of crysta properties on growth temperature. The growtl temperature ranged from 300°C to 800°C. The substrat temperature was controlled at the desired temperature afte thermal annealing at 800°C for an hour. Substrate pretreatment, such as preparing an aluminum layer and surface nitriding, was carried out at the same temperature as the growth process. Table Ⅲ shows the crysta properties of the AlN films estimated by RHEED patterns. Single crystal AlN film with (001)AlN parallel to the substrate, c-axis oriented films, and poly-crystalline films can be obtained at a growth temperature of 700-800°C, 600°C and 300-500°C, respectively. These results indicate that not only the disturbed preparation of the non-crystalline SiN phase between the substrate and AlN film but also the existence of an aluminum layer with periodicity were enough to obtain single crystal AlN film. Namely, the periodicity of the γ-phase of the aluminum which was obtained on the (111)Si 7×7 structure at more than 700°C had a strong influence on the epitaxial growth of (001)AlN. We have previously reported that (001)AlN can be epitaxially grown on c-plane sapphire at the substrate temperature of only 320°C. We thought that the substrate temperature of 600°C would be enough to prepare epitaxial AlN film. However, epitaxial AlN films can not be obtained on (111)Si with a 0.5 atomic layer of aluminum at 600°C. This is why the periodicity of the aluminum layer grown on (111)Si at 600°C is not effective due to the growth of (001)AlN. There is a lack of consensus about the periodicity of the γ-phase of aluminum [9], but we thought that these results, the AlN epitaxial growth on (111)Si with a γ-phase of aluminum, were valuable in order to investigate the periodicity of the γ-phase of aluminum.

Next, AlN was grown on (111)Si with a 0.5 atomic layer of aluminum at the desired temperature after the aluminum layer was grown on (111)Si at 800°C. Table Ⅳ shows the crystal properties of the AlN film estimated by RHEED pattern. Single crystal AlN can be obtained at a temperature of more than 400°C. The crystallinity of single crystal AlN estimated by this RHEED pattern increased with increases in the growth temperature. The epitaxial growth temperature of AlN film grown on (111)Si with a 0.5 atomic layer of aluminum prepared at 800°C is about 300°C lower than that of AlN film grown on (111)Si with a 0.5 atomic layer prepared at the same temperature as that of the deposition process. These results indicate that the γ-phase can not be obtained at 600°C, but the γ-phase or a related phase with similar periodicity, which is useful for (001)AlN growth, can be obtained at 400°C by preparing a 0.5 atomic layer of aluminum on (111)Si at 800°C before the substrate temperature decreases to 400°C due to the start of the deposition process.

Table Ⅳ The crystal properties of AlN films on the (111)Si with 0.5 atomic layer of Al at the various growth temperature. Al layers were grown at 800°C. The twofold circles, and open triangle indicate single crystalline and poly-crystalline phase, respectively.

Ts(°C)	300	400	500	600	700	800
phases	△	◎	◎	◎	◎	◎

(c) Effect on thickness of Al layer on (111)Si

We investigated the dependence of the crystal properties on the coverage or thickness of the aluminum layer on (111)Si. Less than a mono-layer of aluminum on (111)Si will be part of the first layer of AlN after the crystal growth. However, when the AlN film is applied to piezoelectric devices, the aluminum layer under the single crystal film is very valuable. AlN film with a thickness of 100Å was grown on 0.5,1.0 and 5.0 layers and 500Å of aluminum on (111)Si at 800°C. It was found from the RHEED pattern that all of the AlN films had single crystal phases. However, the crystallinity of these films decreased with increases aluminum layer. A.V.Zotov et al. reported that aluminum desorbs from a (111)Si 7×7 structure clean surface after the aluminum adsorbs with about 60 % of the dangling bond for silicon under a substrate temperature of more than 600°C and low aluminum flux rate of less than 0.1Å/s, and three-dimensional growth such as island growth does not appear [9]. All surfaces with a 0.5-5.0 atomic layer of aluminum have almost the same structure in this work. But, we thought that the surface structures of (111)Si with a 0.5 layer and 500Å layer of aluminum were different by considering the aluminum flux rate of 0.5Å/s and the appearance of AlN island growth with the thickness of only 30Å described in the previous section. Unfortunately, we have no information about the periodicity of 500Å aluminum layer on (111)Si at 800°C. If the single crystalline AlN film on (111)Si with 500Å aluminum layer were used for piezoelectric devices the crystallinity of this film would have to be improved by examining the best growth condition.

4. Summary

Aluminum nitride (AlN) films have been prepared on a (111)Si substrate by ECR dual ion beam sputtering. The effects of the initial growth process on film properties were investigated. The results were as follows.
(1) A (001) plane of AlN was epitaxially grown on (111)Si with surface nitriding at a substrate temperature of more than 300°C. This film consists of two types of epitaxial growth with a differential direction in the a-axis.
(2) A (001) plane of AlN can be epitaxically grown on (111)Si with aluminum metallization.
(3) A half atomic layer of aluminum on (111)Si was enough to prepare epitaxial single crystal AlN film.

REFERENCES

1. G.D.O'clock and M.T.Duffy : Appl. Phys. Lett. **23** (1973) 55.
2. L.G.Pearce, R.L.Gunshor and R.F.Pierret : Appl. Phys. Lett. **39** (1981) 878.
3. J.S.Wang, K.M.Lakin and A.R.Iandine : Proc.37th Annu. Frequency Control Symp. (IEEE, New York, 1985) p.144.
4. Y.Chubachi, K.Sato and K Kojima : Thin Solid Films **122** (1984) 259.
5. K.Tsubouchi and N.Mikoshiba : IEEEE Trans. Sonics and Ultrason. **32** (1985) 634.
6. S.Yoshida, S.Misawa, Y.Fujii, S.Takada, H.hayakawa, S.Gonda and A.Itoh : J. Vac. Sci. Technol. **16** (1979) 990.
7. H.Okano, N.Tanaka, Y.Kobayashi, T.Usuki and K.Shibata : Jpn. J. Appl. Phys. **34** (1995) 5172.
8. A.Ishizaka and Y.Shiraki : J. Electrochem. Soc. **133** (1986) 666.
9. R.J.Hamers : Phys. Rev. **B-40** (1989) 1657.
10. A.V.Zotov, E.A.Khramtsova, S.V.Ryzhkov, A.A.Saranin, A.B.Chub and V.G.Lifshits : Surf. Sci. **316** (1994) L1034.
11. M.Yoshioka, K.Takaoka, T.Yao, T.Sueyoshi, T.Sato and M.Iwatsuki : J. Vac. Sci Technol. **B-12** (1994) 2434.
12. K.Nishiyama, T.Hagiwara, A.Takeuchi, A.Kakiuchi, K.Yasutake and K.Yoshii : Ext. Abstr. (43rd Spring Meet., 1995) Japan Society of Applied Physics and Related Societies, 27p-ZB-10 [in Japanese].