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Growth of bismuth silicate thin films by the reaction of SiO_2 layer on silicon

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Crystalline bismuth silicate thin films were prepared on Si by metal -organic chemical vapor deposition. The growth of bismuth silicate film was explained by a steady-state diffusion of Bi_2O_3 in the film grown. The diffusion coefficient of Bi_2O_3 in bismuth silicate films was determined to be $1.5x10^{10}/mm^2/min$, at 750 ℃ Bi_2O_3 layer or particles were formed on surface when the concentration of Bi_2O_3 on the film surface exceeded a critical concentration for nucleation of Bi_2O_3. The capacitance of specimen has increased fivefold over that of the original specimen having a 100nm SiO_2 layer.

1. INTRODUCTION

It is difficult to grow oxide films having useful properties directly on Si wafer, because amorphous SiO_2 layer is formed between the oxide films and Si during growth process. This problem is an obstacle to fabricate capacitor layer in dynamic random access memory (DRAM)[1,2] and ferroelectric nonvolatile RAM(FRAM)[3,4] using the oxide films exhibiting high dielectric constant or ferroelectricity.

In our previous work[5,6], we prepared bismuth silicate films by metalorganic chemical vapor deposition (MOCVD) on the basis of the idea that if SiO_2 layer on Si is changed to a crystalline film of Si compound having a higher dielectric constant and good crystallinity than SiO_2 , this film can be used as a capacitor film in DRAM or as a buffer layer for the growth of other oxide films . We found that the crystalline bismuth silicate film could be formed on Si substrate, but the growth mechanism and electrical property of the film have not been studied.

In this paper, we mentioned in brief the growth mechanism as a steady-state diffusion model and the result of measurement of dielectric property.

2. EXPERIMENTAL PROCEDURE

Bismuth silicate films were grown by MOCVD method. The equipment and growth conditions were described in detail in ref.5. (100) Si wafer having thermally grown SiO_2 layer on surface (100nm, 500nm), were employed as substrates.

The crytalline phases formed in films were identified with x-ray diffraction (XRD). The chemical composition on the surface or along the thickness was analyzed with Auger electron spectroscopy (AES). The capacitance of the films was measured with the impedance analyzer (HP4192A).

3. RESULTS AND DISCUSSION

3.1 Formation of bismuth silicate film

In Fig.1 XRD patterns of the films deposited at various temperatures are shown. The film deposited at 820 ℃ was the polycrystalline cubic phase of $Bi_4Si_3O_{12}$ (JCPDS 33-215), whereas that deposited at 750℃ was a single crystalline bismuth silicate with tetragonal symmetry[6]. It was found that Bi_2O_3 was formed as the growth temperature decreased to 650 ℃ or as the deposition time increased to 180 minutes at 760℃. The formation of Bi_2O_3 particles were also confirmed in SEM and AES observation.

Figure 2 shows the results of XRD on films grown at 750 ℃ for various deposition time. The patterns of films grown for 15 and 30 minutes clearly showed the formation of the single crystalline phase. A part of the single crystalline phase changed to polycrystalline bismuth silicate at deposition time of 45 minutes. It was found that Bi_2O_3 started to form when the deposition time exceeded 45 minutes.

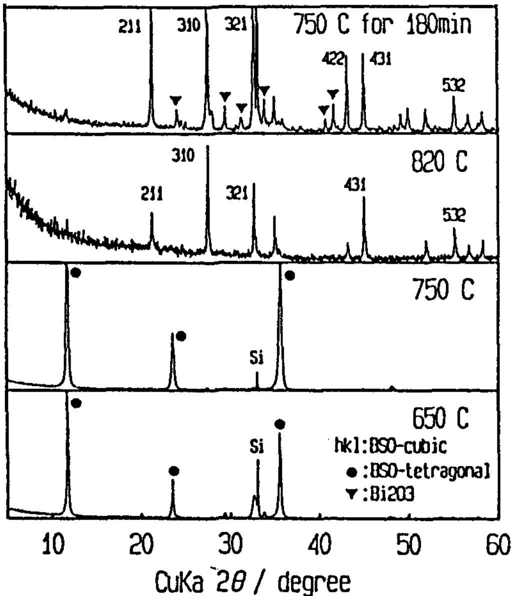

Fig.1 XRD patterns of bismuth silicate film deposited under various conditions

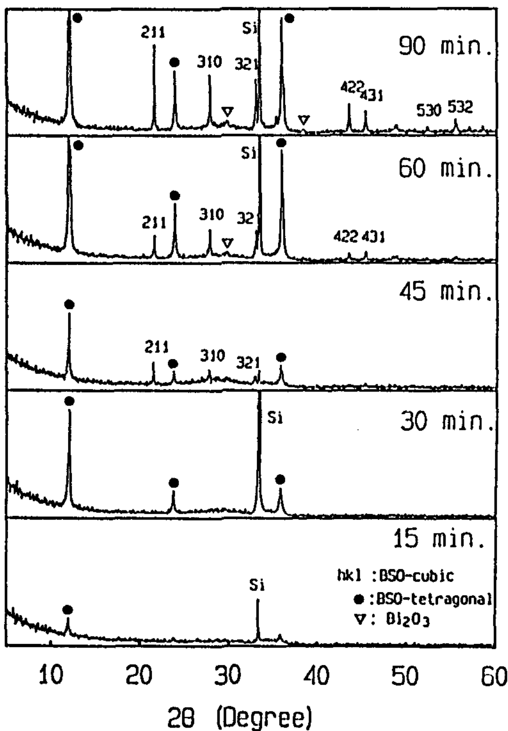

Fig.2 XRD patterns of bismuth silicate films deposited for various time

The result of AES analyses for 100nm specimens indicated that about 90% of SiO_2 layer was changed to bismuth silicate after 30-minute deposition,. whereas SiO_2 layer was completely changed and bismuth silicate contacted with Si metal after 45-minute deposition. However, a small amount of oxygen diffused into Si metal in the latter case. On the other hand, the concentration of Bi_2O_3 on the surface increased with deposition time.

The as-deposited films formed at 750 ℃ were heat-treated at 750℃ and 780℃ for 30 minutes. In the XRD pattern of heat-treated specimen, peak intensity of the single crystalline phase increased as much as about ten times compared with the as-deposited film, which indicated that the crystallinity of bismuth silicate improved markedly upon heat treatment.

3.2 Mechanism of film growth

The thickness of bismuth silicate film was proportional to the square root of the deposition time (Fig.3). This implies that diffusion process dominates the growth of bismuth silicate film. It is considered that the diffusion of Bi_2O_3 takes place from the surface to the interface of bismuth silicate and SiO_2. Figure 4 shows the concentration of Bi_2O_3 as a function of depth from the surface. The concentration gradient of Bi_2O_3 is constant in the bismuth silicate film. Moreover, the concentration

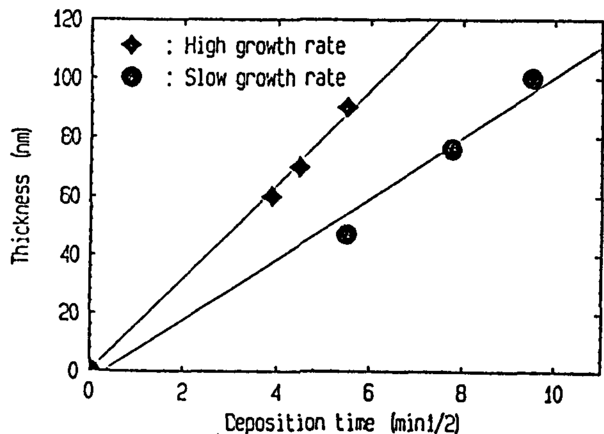

Fig.3 Relation between thickness of film and square root of deposition time

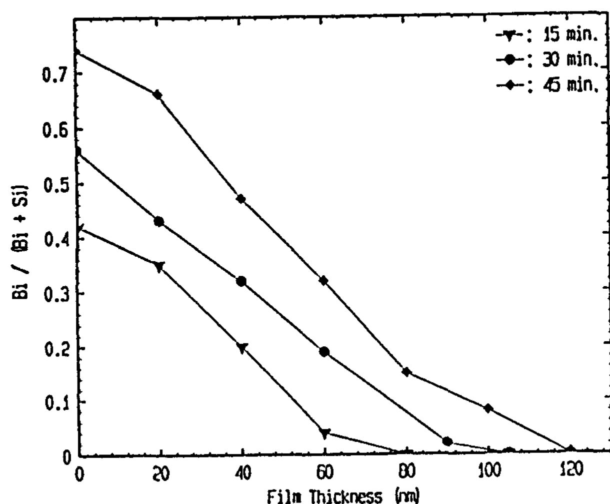

Fig.4 Change of Bi concentration with firm thickness

gradient of Bi_2O_3 is independent of time. These facts clearly mean that the diffusion of Bi_2O_3 is occurred by the steady-state diffusion. In steady-state diffusion, the flux of Bi_2O_3 just below the surface equal to that from the surface to the interface. The same condition was satisfied in the diffusion of oxygen in the oxidation process of Si wafer [7].

Figure 5 is the schematic diagram of Bi_2O_3 concentration profile in the steady-state diffusion model. The flux(J) is given by

$$J = -D\, dC/dX = -D\, Cs/X \qquad (1)$$

where D is the bulk diffusion coefficient of Bi_2O_3 in bismuth silicate. Cs is the concentration of Bi_2O_3 on surface and X is the thickness of bismuth silicate film. The flux of Bi_2O_3 on surface is the same as the deposition rate R= 1.8 x 10^{13} molecules/mm^2/min. Therefore, replacing J with the deposition rate R and rewriting eq.1 then gives

$$Cs \fallingdotseq RX/D \qquad (2)$$

The diffusion coefficient is determined by substituting R, X, and Cs values into the above equation as D=.1.5x10^{10}/mm^2/min.

The concentration of Bi_2O_3 on surface increased with increasing thickness of bismuth silicate layer (Fig.4). If Cs exceeds the critical concentration(Cc) required for the nucleation of Bi_2O_3, the diffusion process of Bi_2O_3 in bismuth silicate is no longer dominant process.

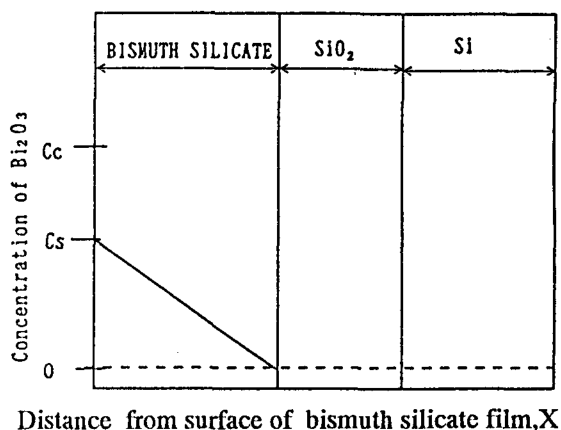

Fig.5 Schmatic diagram of steady-state diffusion model

The formation of Bi_2O_3 on film surface at low temperatures or long deposition time (Fig.1) can be explained by growth mechanism above. At 650℃ of substrate temperature, the diffusion coefficient is lower than that at the higher temperatures, giving rise to a high concentration gradient at the constant flux(J) of Bi_2O_3. Thus, the concentration of Bi_2O_3 on film surface increases to exceed Cc. At 180 minutes of deposition time, the surface concentration of Bi_2O_3 increased above Cc due to the increase of the film thickness.

In the case that bismuth silicate film contacted with Si, Bi_2O_3 were accumulated at film surface because the diffusion coefficient of Bi_2O_3 in Si was much smaller than that in SiO_2. Therefore, Cs became much higher than Cc and Bi_2O_3 layer was grown on film surface.

3.3 Dielectric properties of bismuth silicate film

Figure 3 shows the change in capacitance of specimens with deposition time. Most of the specimens indicated a higher capacitance than the original Si wafer. The specimen deposited for 30 minutes showed the highest capacitance which is over five times higher than that of the original specimen having a 100nm-thick SiO_2 layer. The capacitance decreases when the deposition time exceeds 45 minutes. It was also found that the capacitance of specimen increased by the heat treatment on as-deposited films which improved

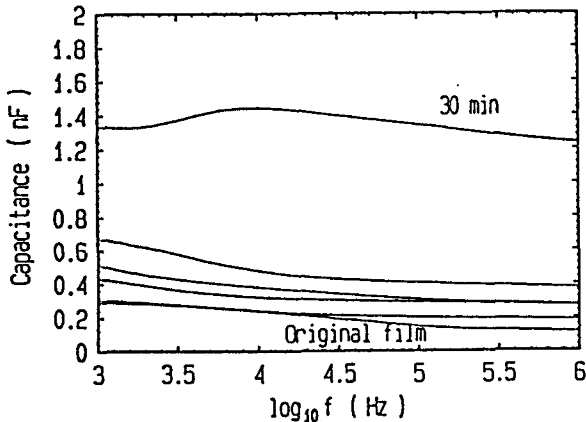

Fig.6 Frequency dependence of capacitance of bismuth silicate film

the crystallinity of bismuth silicate film. The decrease in capacitance of the specimen deposited above 45 minutes may be caused by the diffusion of oxygen atoms into the Si metal and the formation of Bi–rich surface or Bi_2O_3 layer.

4. CONCLUSIONS

This investigation has shown the followings.

(1) The growth mechanism of bismuth silicate films was explained by a steady–state diffusion model of Bi_2O_3. When the concentration of Bi_2O_3 on film surface exceeded the critical concentration for nucleation of Bi_2O_3,Bi_2O_3 layer or particles were formed on the surface.

(2) The diffusion coefficient of Bi_2O_3 in bismuth silicate was 1.5 x 10^{10} /mm^2/min.

(3) The capacitance of specimen increased fivefold over that of the original specimen having a 100nm–thick SiO_2 layer.

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