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A single phase semiconducting Ca-silicide film growth by sputtering conditions, annealing temperature and annealing time

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Abstract Ca films were directly deposited on Si(100) substrates under the same sputtering power and Ar flux by Radio frequency (R.F.) magnetron sputtering system (MS) and were subsequently annealed at 800 °C for 90 min in a vacuum furnace. The structural and morphological features of the resultant films are tested by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive analysis of X-rays (EDAX). The cubic phase Ca_2Si film, the simple orthorhombic phase Ca_2Si film, and the tetragonal phase Ca_5Si_3 film are grown directly and individually on Si(100) substrates, respectively. The experimental results indicate that the selective growth of a single phase Ca-silicide from Ca–Si system of the existence of multiple silicide phases depends on sputtering conditions, annealing temperature, and annealing time. Besides, 800 °C is the adaptive annealing temperature for a single phase Ca-silicide film growth.

Introduction

Recently, semiconducting silicides have attracted much attention for their potential to create new classes of environmentally conscious electronics [1]. Much effort has been made to grow the silicides as well as to develop photoelectronic and thermo-electronic devices for the generation of renewable energy using these materials. Alkaline-earth metal (AEM) silicides are categorized in the materials group. For example, Ca_5Si_3 has been identified by Eisenmann and Schāfer [2] and found to crystallize with the tetragonal Cr_5B_3 type of structure with an energy gap of 0.56 eV. Ca_5Si_3 shows a *p*-type conduction and semiconductor-like behavior [3]. In addition, Ca_2Si has a simple orthorhombic structure and a cubic structure, respectively. ① The orthorhombic structure, which is a stable phase [4] with lattice constants of $a = 0.7667$ nm, $b = 0.4799$ nm, $c = 0.9002$ nm. It is a semiconductor with an energy gap of 1.9 eV [5] (theoretics volume = 0.36 eV), and its electronic band structure is investigated [6–8]. ② The cubic phase Ca_2Si is $a = 0.7016$ nm with an energy gap of 0.56 eV (theoretics volume). Therefore, it is worth clarifying the physical properties of Ca_2Si experimentally [9]. However, it is extremely difficult to grow a single phase film by an interdiffusion reaction of solid phase between the deposited particles and clusters and substrate constituents because Ca has not only the high vapor pressure, but also the existence of multiple silicide phases in the Ca–Si system leads to the simultaneous formation of Ca_2Si, CaSi, $CaSi_2$, Ca_5Si_3 and so on during growth process, and CaSi (18.0 kcal/g atom) is more stable phase than Ca_2Si (12.0 kcal/g atom). Therefore, sol–gel process and powder via were used to make Ca-silicides in the past.

New technique would be required for the growth of a single phase Ca-silicide film on substrates, especially a semiconducting Ca-silicide film. As the enthalpy of formation of Ca_2Si (16.7 kcal/g atom) is higher than that of Mg_2Si (6.30 kcal/g atom), Matsui et al. [10] and Takagi [11] reported the successful growth of the simple orthorhombic phase Ca_2Si layer by the heat treatment of Mg_2Si/Si substrates in Ca vapor. However, it is found that the

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CaMgSi phase is also formed at the Ca_2Si/Mg_2Si interface [12]. In this study, Ca_5Si_3 film and both phases of Ca_2Si films are grown directly and individually on Si(100) substrate for the first time by R.F. MS and by annealing.

Experiment

Si(100) wafers (*p*-type, 7–13 Ω cm) were degreased with acetone and absolute alcohol in the ultrasonic instrument for 20 min, respectively. Then they were rinsed with deionized H_2O, subsequently dried by DHG-9023C blower (dry) kiln.

Ca atoms, ions, and clusters were deposited on Si(100) substrates from a pure calcium (99% purity) target with a diameter of 60 mm (3 in) for 6 min by R.F. MS of JGP560. The sputtering power was maintained constant at 85 W, throughout the experiments. Prior to sputtering, the base pressure was 1.5×10^{-5} Pa. The distance between target and substrate is 80 mm. A 10 sccm Ar (99.999% purity) flux was used as the carrier gas.

(1) The group I samples were prepared in a 1.2 Pa argon only gas ambient. ① Substrates temperature was kept at room temperature before Ca particles and clusters were deposited on the Si(100) substrates. Two pieces of substrates were deposited with 0 or 10 V minus substrate bias, respectively. Then, Si subsequent was deposited on the Ca/Si wafers by direct current (D.C.) magnetron sputtering system of JGP560 in the same ambient gas with about 80 W sputtering power and with 0 or 10 V minus substrate bias on a pure silicon (99.999% purity) target with a diameter of 6 mm (3 in) for 2 min, respectively. The purpose for depositing Si films was to avoid oxidation before the samples were annealed. ② The substrate temperature is kept at 350 °C during sputtering process. Namely, the film was deposited by R.F. reactive sputtering. ③ Two pieces of substrates were deposited at 450 °C with 0 or 10 V minus substrate bias, respectively.

(2) Comparing with the group I samples, the group II samples were prepared in a 7 Pa argon only gas ambient.

(3) Using SGL80 vacuum heat treatment oven, all of the deposited films were annealed at 800 °C for 90 min. Prior to annealing, the base pressure was 4.2×10^{-4} Pa. During the heat treatment, the air pressure in the vacuum chamber was kept at between 1.0×10^{-3} and 2.3×10^{-4} Pa.

The structural and morphological features of the resultant films were characterized using D/MAX-2200 X-ray diffraction (XRD) CuK_α ($\lambda = 1.54$ Å), HITACHI S3400N scanning electron microscope (SEM) at an acceleration voltage of 30 kV and NORAN System-SIX energy dispersive analysis of X-rays (EDAX).

Results and discussion

As shown in Figs. 1a, b, c, e and 2a, b, e, a single phase Ca-silicide or a dominant phase Ca-silicide is grown to form by annealing at 800 °C for 90 min. Here, depending on the experimental procedure explains the selective growth.

Sputtering nucleation

Initial sputtering stage

The intrinsic defect on Si substrates may be responsible for surface roughening and surface defect density so as to

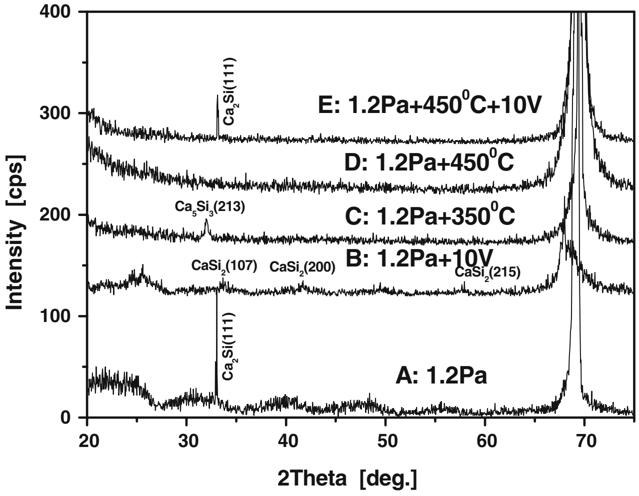

Fig. 1 The XRD patterns of the group I samples

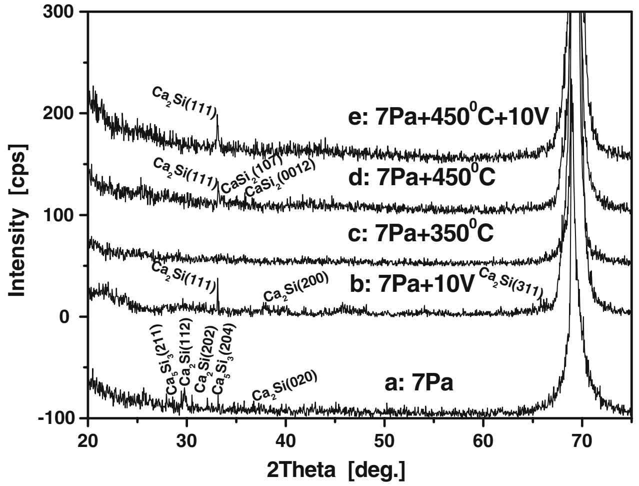

Fig. 2 The XRD patterns of the group II samples

determine the nucleation density of a Ca-silicide in a Ca-silicides system. By sputtering, the absorbed ions, atoms, and clusters on substrate surface diffuse along their incident direction even if a part of particles and clusters are fallen from substrate surface desorption. Due to the experimental technologies by sputtering under the different negative substrate bias, reactive sputtering at the different temperature and reactive sputtering under the negative substrate bias are used so that the diffusivity of particles and clusters in substrates is the different, a sample under a sputtering condition relative to other sample, has the different surface texture, interface, growth thickness, depositing thickness, nucleation density and so on. The diffusivity of particles and clusters in a sample only by sputtering ought to be lower than those using reactive sputtering and sputtering under the different negative substrate bias. And, it must be noticed, the heat energy only by sputtering by energetic particles and clusters cannot suffice the temperature for annealing. Thus, the grown thickness of films is increased with inflicting minus substrate bias, providing reactive sputtering and both applying simultaneity. In addition, a sample by reactive sputtering is equal to the sample made by sputtering and annealing simultaneously. Duo to Ca is a high vapor pressure element, even if there are the remnant particles and clusters on substrates, will also be vaporized during reactive sputtering. Thus, all of the films by reactive sputtering may be transformed into Ca–Si compound.

Bombardment stage

Bombarding induces the change of lattice parameter of films and increases binding power of films which moves the deposited formerly particles and clusters to landscape orientation to improve compactness of film [13, 14]. Bombarding by energetic particles and clusters on the surface of substrates should make a Ca-silicide to nucleate in twice. And, the different sputtering conditions make the different bombarding intensity. Thus, comparing with other samples, a sample has the different surface texture, interface, growth thickness, depositing thickness and so on. Simultaneously, shadowing effect may influence the roughening of Ca-silicides films. Thus, a formed Ca-silicide system by the initial sputtering is transformed into other Ca-silicides system by bombarding. Finally, those films, which the temperature of substrates is kept at room temperature before sputtering, only Ca particles and clusters are accumulated with prolonging of deposition time, and the deposition thickness is increased with prolonging of sputtering time and then it decreases since it has come to peak. Other films, which are deposited by reactive sputtering, the grown thickness is increased with prolonging of sputtering time before Ca-silicides systems are homeostasis.

As mentioned above, the mechanism for depositing Si by D.C. MS is similar with the mechanism for depositing Ca by R.F. MS. The deposited Si films on the surface of Ca/Si films at room temperature will be formed interlayer films. However, it must be noticed that bombarding by Si particles and clusters on the surface of substrates should make a Ca-silicide on films to nucleate in twice, and should also make nucleation between Ca films and Si particles and clusters. Thus, the Ca-silicides system of a film is translated into other Ca-silicides system because of sputtering of Si particles and clusters. In that way, the films by reactive sputtering are the monolayer film structure. Therefore, 10 pieces of films have the different Ca-silicides system by the different sputtering conditions.

Annealing nucleation

Those films are made under the same annealing conditions. As shown in Figs. 1 and 2, the selective growth of a particular phase is mainly triggered by a specific interface composition, and is governed by the diffusion flux to the interface [15], which is depended on sputtering conditions, and shows the multiple silicide phases in Ca-silicide system is reconstructed, is grown selectively by annealing. The growth process is influenced by the strong growth orientation of the grown crystal grains and stress mismatch in crystal lattice. However, why do the XRD patterns of the most results show only a diffraction peak? As shown in Fig. 3a and b, which come from the samples of Fig. 1c and e, confirms that two of samples consist mainly of calcium except silicon. In addition, ① as shown in the cross-sectional SEM images (the below images) of Fig. 4b, which comes from the sample of Fig. 1c. The starting films of Sample “C”, Sample “D” and Sample “E” have the same structure, which are the monolayer film structure. Interdiffusion ability between deposited particles and clusters and substrate constituents is increased with increasing of substrate temperature so as to increase growth thickness of the starting film during reactive sputtering. And, a 10 V minus bias is put on the substrate when the starting film of Sample “E” is made during sputtering. Thus, the thickness of Sample “E” is the thickest. ② As shown in the cross-sectional SEM images (the below images) of Fig. 4, the thickness of the film of Fig. 4c is the thinnest. Depending on the XRD pattern (Fig. 2a) and the plan-view SEM image (the above image of Fig. 4c) of the sample of Fig. 4c can show that there is a Ca-silicide film is grown on the resultant film. Therefore, in Ca–Si system, two pieces of films are consisted of the cubic phase Ca_2Si and the tetragonal phase Ca_5Si_3, respectively.

Growth behavior of a Ca-silicide in a Ca-silicide system is dominated by diffusion effect and oriented growth mechanism, as well as coarsening mechanism, induced by

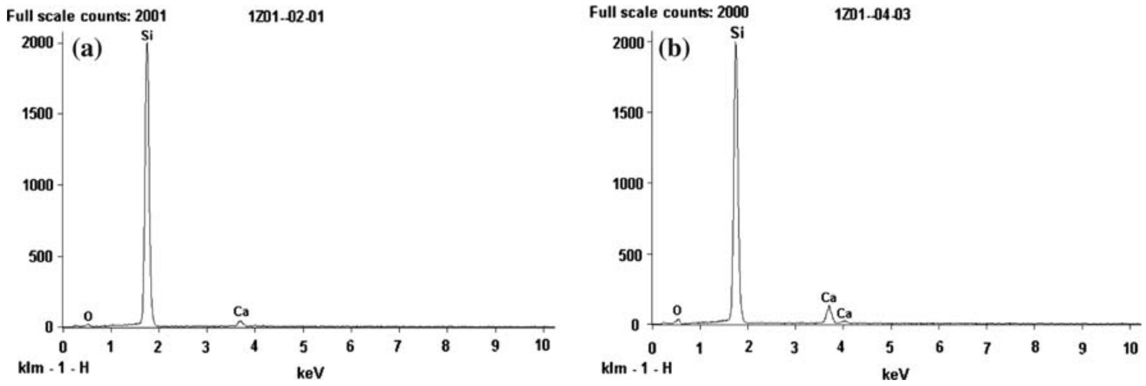

Fig. 3 Energy spectrum images of the samples. **a** The starting film was deposited by reactive R.F. sputtering in 1.2 Pa argon gas ambient at 350 °C. **b** The starting film was deposited by reactive R.F. sputtering in 1.2 Pa argon gas ambient at 450 °C with 10 V minus substrate bias

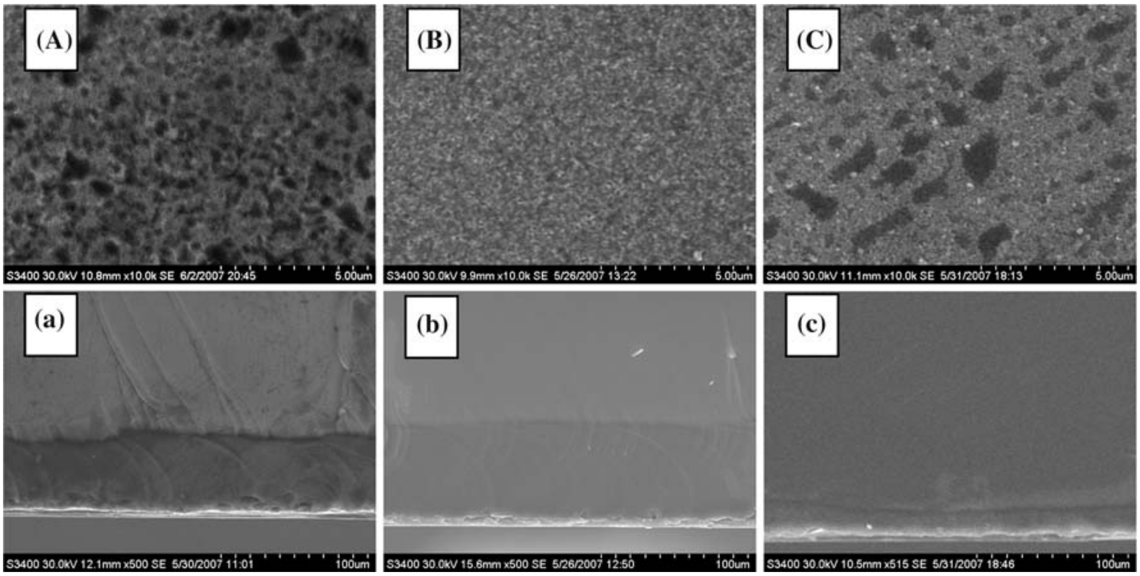

Fig. 4 The plan-view and cross-sectional SEM images of a single phase semiconducting calcium silicide. **A** (**a**) The starting was deposited by R.F. sputtering in 1.2 Pa argon gas ambient. **B** (**b**) The starting film was deposited by reactive R.F. sputtering in 1.2 Pa argon gas ambient at 350 °C. **C** (**c**): The starting film was deposited by R.F. sputtering in 7 Pa argon gas ambient

sputtering conditions. Firstly, ① as shown in Fig. 1a and b, all of resultant films come from the interlayer structure by sputtering with 0 or 10 V minus substrate bias, respectively. The energy of sputtering particles and clusters is increased with inflicting minus substrate bias so as to enhance bombardment intensity, improve diffusivity and change surface texture, interface, deposition thickness and growth thickness. In addition, Si film on sample surface can restrict some Ca particles and clusters to be evaporated in the annealing nucleation stage even if Ca has high vapor pressure, and may make the particles and clusters in possession of the powerful active diffusion energy so as to improve diffusivity because of the limit of Si film on surface and no out-diffusion of Si atoms from the substrates. ② R.F. sputtering condition is translated into reactive R.F. sputtering condition. As shown in Fig. 1d and e, the grown film is translated from amorphous film into the cubic phase Ca_2Si film when the substrate is inflicted minus bias during sputtering process. As comparison, reactive R.F. sputtering can improve diffuse ability so as to increase growth thickness and nucleation density of the starting film during reactive sputtering. In addition, as shown in Fig. 1a and e, nucleation density of the starting film by reactive sputtering is not only increased, but also reconstructing in twice heat treatment may improve the purity of the crystal compounds by annealing. Secondly, as shown in Fig. 1c and d, the grown film by annealing is translated from the tetragonal phase Ca_5Si_3 film into amorphous film when the temperature of substrates is increased from 350 to 450 °C during sputtering process. Two pieces of resultant films come from the monolayer structure by reactive sputtering. The growth thickness of the starting film is increased with increasing of substrate temperature during reactive sputtering. Thus, a film with the different nucleation density and growth thickness during sputtering will influence its growth orientation during annealing process. Therefore, growth thickness of films on Si(100) substrates play a role of controlling the morphological evolution and the lattice mismatch stress. Thirdly, as shown in Fig. 1a and c, the growth film is translated from the cubic phase Ca_2Si film into the tetragonal phase Ca_5Si_3 film when the starting films are the different structure during sputtering process. Growth thickness by reactive sputtering is thicker than that only by sputtering. As shown in the cross-sectional SEM images (the below images) of Fig. 4a and b, the thickness of the Ca_5Si_3 film is thicker appreciably than that of the cubic phase Ca_2Si film. Thus, it explains an amount of Ca particles and clusters are not only evaporated from monolayer film surface by restructuring by annealing, but also the grown crystal is changed because two pieces of films have the different starting structure. Therefore, the growth mechanism depends strongly on the structure of the starting films, boundary conditions and not simply on the free energy of formation [16]. Finally, ① As shown in the plan-view SEM image (the above image) of Fig. 4c, percentage area of the simple orthorhombic phase Ca_2Si film is the main block on the resultant film, which is accordant with the XRD pattern of Fig. 2a. ② As shown in Figs. 1a and 2a, the grown crystal is translated from the cubic phase Ca_2Si film into the simple orthorhombic phase Ca_2Si film when sputtering Ar pressure is changed from 1.2 to 7 Pa. Decreasing working pressure is equal to increasing sputtering power or inflicting minus substrate bias. Thus, the films by sputtering in 7 Pa have the different surface texture, interface, growth thickness, depositing thickness, nucleation density and so on. Therefore, the resultant films, which come from the different sputtering conditions have the very different growth orientation during annealing process.

Relaxation of stress by annealing in the boundary conditions so as to increase stoichiometric ratio and optimize crystal quality. Figure 4a, b and c comes from the samples of Figs. 1a, c and 2a, show the plan-view and cross-sectional SEM images of the Ca-silicides (the cubic phase Ca_2Si film, the tetragonal phase Ca_5Si_3 film and the simple orthorhombic phase Ca_2Si film). As shown in the plan-view SEM images (the above images), the diminutive grains are stacked on the surfaces of substrates, exhibits the densest surface structure. However, as shown in the plan-view SEM image of Fig. 4a, the surface of the cubic phase Ca_2Si film is not even and there are voids observed. In addition, as shown in the cross-sectional SEM images of Fig. 4a and c, the film thickness by sputtering in 7 Pa is thinner extraordinarily than that in 1.2 Pa. Therefore, between the growth thickness and surface character of films by annealing and bombardment intensity by sputtering will be completed in future. The growth procedure shown in this study would open the possibility of the growth of a variety of binary and ternary "environmentally friendly semiconductors".

Conclusion

Substrates are exposed to Ca metal, and silicidation reaction takes place on the surface of substrates by interdiffusion between deposited particles and clusters and substrate constituents. (1) The cubic phase Ca_2Si film, the tetragonal phase Ca_5Si_3 film and the simple orthorhombic phase Ca_2Si film are grown to form directly and individually on Si(100) substrates at 800 °C for 90 min, respectively. (2) Sputtering conditions provide a basic guideline for the selective grown because it is close contacted with boundary condition, morphological character, bombardment defect, nucleation density, surface texture, interface, growth thickness, depositing thickness and so on. (3) Annealing temperature and annealing time is the principal factor because they are close contacted with diffusivity. Besides, 800 °C is the adaptive annealing temperature for a single phase Ca-silicide film growth.

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