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The effect of composition on surface morphology, formation mechanism and pinhole generation of cosputtered ytterbium silicide

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ABSTRACT

The surface morphology including pinhole and silicide formation mechanism of codeposited ytterbium silicide films are investigated with various compositions of Yb and Si. Film properties depend on the growth mode of the deposited films. At Si compositions more than half of the stable phase of ytterbium silicide, films have a rough surface with islands of ytterbium silicide formed by the Stranski–Krastanov and Volmer–Weber growth mode. At Si composition below half of the stoichiometic value, films grow in a layer by layer, Frank–van der Merwe mode, with a smooth surface. The transition of the formation mode is due to a trade-off in the dominance of the reaction between the internal atoms in the deposited films or between the deposited films and the substrates. A Si composition of 0.59 provides the smoothest surface with roughness of 1.13 nm in root mean square value and no observed pinholes. Ytterbium silicide films are deposited with a 5% composition tolerance by cosputtering and forming at 450 °C in a conventional furnace.

1. Introduction

Rare earth (RE) metal silicides ($ErSi_{2-x}$, $YSi_{1.7}$, $TbSi_{1.7}$, $YbSi_{2-x}$) are of interest as one of the promising source/drain materials in nano scale metal oxide silicon field effect transistors because of their low temperature formation, low resistivity and low work function difference to n-type Si [1–4]. Additionally, the lattice constant of RE silicides which have the hexagonal AlB_2 crystalline structure group, is well matched to (111) Si — the mismatch of lattice constant is 1.59% [5]. This provides an opportunity for epitaxial growth on Si with good electrical properties. However, pinhole and defect generation of RE silicides are major issues for their use in real applications because pinholes degrade electrical properties such as increase of the Schottky barrier height or junction leakage [6–8]. Pinhole formation in these materials is closely related with the defective formation of disilicides. Perfect AlB_2 structures have a ratio of 1:2 between Al and B atoms, however, the actual composition ratio of RE metal to Si has been shown to be in the range of ~1.7 to ~1.85. The transition from AlB_2-type Yb silicide to Th_3Pd_5-type Yb silicide has been suggested to explain this discrepancy. However, this stoichiometry could also be due to Si vacancies in the AlB_2-type crystal structure [9]. These vacancies, about one atom per six sites, are closely related to the movement of Si atoms as the dominant diffusion species in RE silicides [10] and make the preferred growth mode nucleation-type growth, such as Volmer–Weber (VW) or Stranski–Krastanov (SK) growth modes of defective disilicides i.e. ~$RESi_{1.7}$ [11,12]. Generally three kinds of growth mode – VW, SK and Frank–van der Merwe (FM) – exist in crystal growth on the surface as shown in Fig. 1. FM mode is that films grow layer by layer and VW and SK modes are three dimensional (3D) growth. These non planar growth modes generate defective surfaces and pits easily [13].

Three kinds of pinhole generation mechanisms are often suggested in RE silicides. The first is contamination of the Si surface [6]. The contaminants on the Si surface disturb the reaction between the RE metal and Si so that RE silicides are formed unevenly on the surface. Uneven silicides are known to generate pinholes [14,15]. This kind of mechanism can be mitigated by processing in ultra high vacuum (UHV) systems and treating surface carefully [16]. The second mechanism is island-type growth of the RE silicide at the interface between the RE metal and Si [17,18]. In nucleation-type growth, discontinuous silicide layers were formed between RE metal and Si at an early stage of growth and these silicide islands retard reaction by suppressing diffusion of Si. As a result, the uneven interface generates pinholes [17,18]. The third mechanism is the partial delamination of RE silicides due to film stress [19]. Even if the silicide layer is formed uniformly, particularly when the RE silicide was formed at low temperature, severe compressive stress can occur by fast updiffusion of Si through the silicide and formation of an amorphous mixed layer with diffused Si and RE metals on top of the silicides. This stress lifts RE silicide layers locally, limiting the silicide formation in the lifted region [20]. Thus, in the second and third mechanisms, the pinhole generation is due to nonuniform diffusion of Si from Si substrate. As a result, to obtain pinhole free films on clean substrates one should minimize the need for Si diffusion from the substrate. One of the most useful methods to minimize consumption of substrate Si is the deposition of an α-Si layer on top of the RE metal. This

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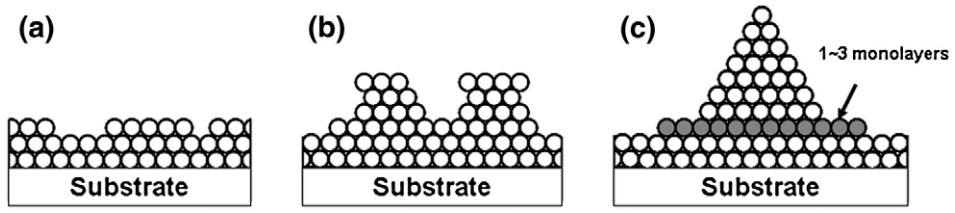

Fig. 1. Schematic diagram for growth mechanism (a) Frank–van der Merwe (FM), (b) Volmer–Weber (VW), (c) Stranski–Krastanov (SK).

method supplies additional Si atoms to form the silicide so as to reduce consumption of Si atoms from the substrate (of course, this will still require the diffusion of Si from the sputtered layer) [21]. Another suggested method based on uniform diffusion is the deposition of an amorphous Si film between the substrate and the deposited RE metals [22]. In both methods, the reaction between two deposited layers is extremely important and so pinhole generation is sensitive to the thickness ratio between α-Si and RE metals [18,22]. It is also sensitive to the nature of the reaction between the deposited Si and the RE metal. These arguments suggest that a more effective way to avoid pinhole generation would be to directly deposit RE silicide films with the stoichiometry of stable phase of RE metal silicides. However, the flux ratio of RE metal and Si is not easy to control precisely. Several calibration processes are required to obtain process conditions in a UHV molecular beam expitaxy system [16].

This work investigates the surface morphology and formation mechanism of codeposited ytterbium silicide films with varying stoichiometry deposited on (100) Si in a conventional sputtering system. Even though the lattice constant of this rare earth silicide is very well matched with lattice constant of (111) Si, (100) Si is preferred in electronic devices because of carrier mobility considerations [23].

2. Experiment

Codeposited ytterbium silicide films were obtained by sputtering Yb and Si simultaneously using an AJA ATC 2000 sputter deposition system to change Yb and Si ratio of films on p-type (100) silicon. The wafers were cleaned by Piranha solution ($3H_2SO_4 + 1H_2O_2$ at 120 °C) for 30 min to remove organic residue, then a 50:1 deionized water diluted HF solution for 1 min to remove the resultant chemical oxide, then loaded into the deposition system load lock immediately. After loading into the deposition chamber, the system was pumped to a base vacuum of 6.67×10^{-5} Pa. All depositions were done in 5.5 grade Ar at 0.13 Pa. The substrates were nominally at room temperature.

To find the dependence of the film properties on the composition of the films, the Yb deposition power was varied from 20 W to 100 W. Yb was found to have a wider range of deposition rates than Si. The Yb deposition rate was found to vary linearly with power as shown in Table 1. Si was deposited at 360 W by RF sputtering in an Ar environment under the same pressure, producing a deposition rate of 0.086 nm/s when deposited separately. The deposition rate of co-deposited Yb and Si agrees well with the sum of deposition rates of the respective materials. To verify the results, the ytterbium and silicon concentrations were measured through Rutherford Backscattering Spectroscopy (RBS) with 2.0 MeV He^+ ions. The composition of Si in codeposited $YbSi_x$ films before anneal ranged from $x = 2.09$ at 20 W to $x = 0.40$ at 100 W as shown in Table 1. As expected, the RBS results for the composition ratios of as-deposited films correspond well to deposition ratios of two materials. The difference between two results was 5.2% at most.

The thickness of the co-deposited film was about 75 nm for all samples. An anneal was performed 450 °C for 30 min under a nitrogen and argon ambient. Then the annealed samples were placed into $3HCl + 1HNO_3$ (aqua regia) for 10 min to remove unreacted Yb and Si mixtures. For the as-deposited samples as well as those annealed below 400 °C, the deposited films were completely removed in aqua regia due to the abundance of unreacted metals. At 400 °C and above, a ytterbium silicide film was formed. The pinhole formation of ytterbium silicide was inspected by JEOL-6500 field emission scanning electron microscope (SEM) and the surface roughness was then measured in tapping mode by atomic force microscope (AFM) using a Digital Instrument 3000 AFM. X-ray diffraction (XRD) patterns were measured using the Bruker-AXS microdiffractometer with a Cu kα X-ray source to examine the crystalline structure of ytterbium silicide.

3. Result and discussion

The SEM and AFM images of various compositions of ytterbium silicide are shown in Figs. 2 and 3. When the composition is $YbSi_{2.09}$, which is close to the stoichiometry of perfect structural disilicides composition ($RESi_2$), no distinct triangular or pyramidal shaped pinholes, which are typical pinhole shapes in rare earth silicides [18,23,24], are observed on the surface. The root mean square (RMS) of surface roughness, however, is 12.4 nm. This large value of the roughness may be due to 3D islands of the silicide. Two kinds of islands are observed on the surface of annealed ytterbium silicide films as shown in Fig. 2(a) and (b); the first is small islands which correspond to the VW growth mode. In the VW mode small clusters form islands on the surface because the cohesive force between clusters is stronger than adhesive force to the interface [25]. These small islands grow on any surface irrespective of substrate as shown in Fig. 2(b). However the islands formed in the middle of wetting layers – 1–3 monolayers – become seeds of SK mode growth as shown in Fig. 1(c). The shape of the islands is arbitrary in the SEM image as shown in Fig. 2(a). The length of islands ranges from 30 nm to 300 nm on SEM images while the height of islands ranges from 25 nm to 42 nm from AFM analysis as shown in Fig. 2(b). The length variation of islands is generally larger than that of height. This suggests that the islands coarsen laterally on the surface, i.e., the single crystal grains about several nanometers in dimension coarsen and form polycrystalline grains ranging from 25 to 42 nm and those polycrystalline grains agglomerate and grow laterally. The other particular type of island observed in the micrographs corresponds to cone shaped 3D growth which is typically seen in the

Table 1
Physical properties of codeposited films by various deposition power of ytterbium.

Yb deposition power [W]	Yb deposition rate [Å/sec]	Yb + Si deposition rate [Å/sec]	Si composition x in $YbSi_x$	Grain size [nm]	Surface roughness [nm]
20	0.396	1.23	2.09	7.15	12.42
25	0.503	1.37	1.71	6.17	11.34
35	0.707	1.61	1.28	5.69	10.71
50	1.121	1.94	0.75	5.56	6.73
75	1.481	2.34	0.59	6.09	1.18
100	2.194	3.04	0.40	6.39	2.43
Single Yb				5.20	3.22

Deposition rate of ytterbium and co-deposited ytterbium silicide films, Si composition of as deposited ytterbium silicide by RBS analysis, grain size by XRD analysis and surface roughness by AFM analysis.