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Silicidation of Mo-alloyed ytterbium: Mo alloying effects on microstructure evolution and contact properties

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Abstract—In this study, we investigated the effects of Mo addition to Yb as a contact material with Si for metal–oxide-semiconductor field-effect transistors (MOSFETs) to mitigate oxidation problems, a persistent problem for rare-earth metal-based contacts (such as Yb/Si and Er/Si). Our thorough materials characterization using transmission electron microscopy and X-ray diffraction unravels Mo segregation during silicidation and its effect against oxidation. I–V characteristics, measured from Schottky diodes produced from the samples, reflect such microstructure evolution and demonstrate a strong improvement in contact properties at high temperatures.

Keywords: Yb silicide; Mo-alloyed ytterbium; Epitaxial layer; Schottky barrier height; Thermal stability

1. Introduction

Establishing a good electrical contact between metal and semiconductor is critically determined by interface-related materials phenomena. For metal–oxide-semiconductor field-effect transistors (MOSFETs), improving the contact properties between metal and silicon becomes increasingly important, as the contact area shrinks rapidly with scale-down of the device. This has fueled the drive to find a new contact material with a low contact resistance or to enhance the contact properties of the conventional nickel-based contact. In particular, rare-earth (RE) metal silicides (Er, Yb, etc.) have recently received a renewed attention as new contact materials, since they have a very low Schottky barrier height (SBH) on n-type silicon (0.2–0.4 eV) [1–6].

Among several RE silicides, ytterbium silicide deserves much attention due to its some favorable characteristics for low SBH applications [3–6]. For example, a study done by Zhu et al. estimated the Schottky barrier height (SBH) for the Yb silicide contact with n-type Si to be as low as 0.27 eV by estimation from SBH obtained from Yb silicide with p-Si [6]. In our previous study, we carried out a preliminary study on the kinetic aspect of this material. We reported that Yb silicide grew with epitaxial relations on Si (0 0 1) with no indication of pinhole formation [7]. Such epitaxial silicide is expected to be beneficial for contact properties, since it is likely to form good metal/semiconductor interface [8].

Nevertheless, it is well-known that rare-earth silicides suffer from severe oxidation at elevated temperatures, which hampers the wide-spread employment of this contact material. In the present study, we examined the possibility of using Yb alloyed with such a refractory metal as Mo to mitigate the oxidation problem. The Mo addition to Yb offered a unique opportunity to explore some interesting interplay between the elements (Yb, Si and Mo) and its sensitive impacts on the contact properties. We first investigated the degradation of Yb/Si contact due to oxidation at high temperatures and then compared with the high temperature behavior of Mo-alloyed Yb/Si contact. Combining several transmission electron microscopy (TEM) analytical techniques helped us to unveil some intriguing materials reactions in the Mo-alloyed sample. Characterization of the electrical properties (sheet resistance and Schottky barrier height) of the samples annealed at different temperatures

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confirms that the Mo addition critically improved the contact properties at high temperatures.

1.1. Experimental procedure

For the Yb sample, Yb was deposited on a n-type silicon (0 0 1) substrate with a resistivity of 1–10 ohm cm using a radio frequency (rf) magnetron sputtering system. For the Mo-alloyed sample, Yb and Mo were co-sputtered from separate targets, and the composition of Mo was found around 20 at.% from an EDS analysis. To remove the native oxide of the silicon substrate, the wafer was dipped in 1% HF solution and then rinsed with deionized water. After drying with N_2 gas, we loaded the cleaned wafer immediately into the RF sputtering chamber. Prior to deposition, the base pressure of the chamber was $\sim 2 \times 10^{-7}$ Torr. The films were deposited at room temperature and a working pressure of 9 mTorr in Ar ambient. Subsequently, a tantalum nitride (TaN) capping layer with the thickness of 50 nm was deposited without breaking vacuum to minimize oxidation. To measure SBH, we fabricated Schottky diodes by patterning circular dots (diameter: 50 μm) of Yb and Yb(Mo) alloy via lift-off. To form Yb silicide, the deposited samples were annealed using rapid thermal annealing (RTA) at various temperatures (300–800 °C) for 1 min in N_2 ambient (the base pressure was $\sim 3 \times 10^{-3}$ Torr). For materials characterization, we utilized transmission electron microscopy (for microstructure analysis, JEM-2100F operating at 200 keV; for chemical analysis, JEM-ARM200F operating at 200 KeV) and X-ray diffraction (X'pert PRO-XRD, 2T-omega, Cu κ_α: $\lambda = 1.5406$ Å). The sheet resistance was measured using four-point probe method. In addition, the electrical characteristics of the Schottky diodes were examined using an HP semiconductor parameter analyzer (HP4145B) at room temperature.

2. Results and discussion

2.1. Microstructure analysis

We first examined materials reactions upon annealing using XRD, as shown in Fig. 1. Comparing the XRD data for the two sample sets, Yb and Yb(Mo), discloses that the Mo-alloyed sample has a higher stability against oxidation at high temperatures. For the Yb sample, upon annealing at a low temperature (300 °C), the Yb (1 1 1) peak has disappeared, which suggests solid-state amorphization, consistently with the results reported in other studies on the rare-earth metal/Si system [9–12]. The (1 0 1 0) peak of $YbSi_{2-X}$, with the hexagonal AlB_2 crystal structure, appears upon annealing at temperatures above 400 °C. The peaks of $YbSi_{2-X}$ become stronger upon annealing at a higher temperature, suggesting that the thickness of the $YbSi_{2-X}$ layer increased. Upon annealing at 700 °C, however, the peaks of the Yb oxide phase (Yb_2O_3) emerge and the silicide peak diminishes drastically. For the Yb(Mo) sample, strong $YbSi_{2-X}$ peaks appear at 600 °C and remain stable up to 800 °C. It should be noted that silicidation reaction took place at a higher temperature in the alloyed sample. In addition, there is no indication of oxide peaks up to 800 °C annealing, suggesting a significant improvement in thermal stability against oxidation.

Further microstructure analysis using TEM unraveled quite interesting contrasts between the pure and Mo-alloyed samples in silicidation behavior. First, the pure Yb sample displays a similar series of microstructure evolution observed in our previous study, starting from solid-state amorphization to the formation of an epitaxial silicide layer, as shown in Fig. 2a–e. Our further analysis on the epitaxial silicide revealed two epitaxial relations (A type: $(1\,0\,1\,0)YbSi_{2-X}//(0\,0\,1)Si$ and $[0\,0\,0\,1]YbSi_{2-X}//[1\,1\,0]Si$; B type: $(1\,0\,1\,0)YbSi_{2-X}//(0\,0\,1)Si$ and $[0\,1\,1\,0]YbSi_{2-X}//[1\,1\,0]Si$), consistent with the results of our previous study [7]. (For further information on the epitaxial relations, see the schematic diagram shown in Supplementary Information (Fig. S1).) However, the sample annealed at 600 °C starts to show some microstructure features indicative of oxidation (Fig. 2f). An amorphous layer with a bright contrast formed at the top part of the silicide layer, suggesting that oxidation possibly started from the top. Annealing at a higher temperature (700 °C) prompted a disruption of the epitaxial layer, as shown in Fig. 2g. It appears that the oxidation process consumed some regions of the Yb silicide layer, consistent with the emergence of the oxide peaks in the XRD data (Fig. 1a). (Note that in the image, the left side was fully consumed by oxidation while the right side still remains as silicide.) Annealing at 800 °C brought about a complete oxidation, as shown in Fig. 2h. This result highlights the vulnerability of Yb silicide against oxidation. We found that several factors such as the ambient and the barrier also influenced oxidation resistance. For example, samples with a TiN barrier, which was known to have barrier properties inferior to that of TaN, showed oxidation at much lower temperatures and in a greater extent (TEM images shown in Fig. S2).

For the Mo-alloyed sample, the reactions occurred at temperatures somewhat higher than those for the pure Yb sample. Upon annealing at 300 °C, full amorphization of the Yb(Mo) alloy film occurred, as shown in Fig. 3a. Upon annealing at 400 °C, the epitaxial Yb silicide has just nucleated at the interface between Yb(Mo) alloy and Si, as shown in Fig. 3b. Fig. 3c shows the growth of epitaxial Yb silicide upon annealing at 500 °C, a temperature significantly higher than that needed for the Yb sample. The high resolution electron micrograph, shown in Fig. 3c, displays the same epitaxial relations as those of the Yb sample (A-type: $(1\,0\,1\,0)YbSi_{2-X}//(0\,0\,1)Si$ and $[0\,0\,0\,1]YbSi_{2-X}//[1\,1\,0]Si$, B-type: $(1\,0\,1\,0)YbSi_{2-X}//(0\,0\,1)Si$ and $[0\,1\,1\,0]YbSi_{2-X}//[1\,1\,0]Si$). Upon annealing at 600 °C, the epitaxial layer grew somewhat thicker up to around 10 nm, and the remaining part of the layer changed to a microstructure which is composed of randomly-shaped small grains. A careful phase analysis of the small grains using high resolution electron micrographs suggests that they are aggregates of Mo silicides ($MoSi_2$, Mo_5Si_3) and Yb silicides (Yb_3Si_5 and $YbSi_{2-X}$). It should be noted that this microstructure, with the epitaxial silicide layer nearly intact, remains stable up to 800 °C, with no indication of such a disruption due to oxidation as observed in the pure Yb sample. This result is also consistent with the XRD result that the Yb silicide peaks remain strong up to 800 °C. This result clearly demonstrates that alloying with Mo improved greatly the oxidation resistance of the silicide.

To further understand the effects of Mo alloying, we, using EDS, delved into the distribution of Mo, Yb, and Si, as shown in Fig. 4. Fig. 4 shows a high-angle angular dark field (HAADF) image and EDS elemental maps for Mo, Yb, and Si. An interesting feature captured in the