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Characterization of ytterbium silicide formed in ultra high vacuum

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Abstract. The formation of ytterbium silicide fabricated by annealing at 480 °C for one hour has been studied by means of high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS). The annealing process has been performed under ultra high vacuum (UHV) conditions. The formation of an amorphous silicide layer was observed between the Yb-layer and the silicon substrate in the as-deposited sample. Ytterbium silicide observed after annealing consists of two different layers: crystalline and amorphous ones. The studies confirmed that the formed crystalline layer is of the YbSi_{2-x} phase, however, the structure is different from the hexagonal AlB₂ type.

1. Introduction

Ytterbium silicide has the lowest electric work function [1] amongst the rare-earth (RE) metals (Gd, Dy, Ho, Er) already used for low Schottky barrier [2] applications. Therefore, ytterbium silicide is a very promising material as a silicide source/drain in n-channel Schottky Barrier (SB) MOSFETs [3]. The most commonly used method of the ytterbium silicide fabrication is a thermal annealing of the Yb-film deposited on silicon. Interdiffusion of ytterbium and silicon atoms during annealing at the metal/silicon interface makes the solid-state reaction possible. There are some reports on fabrication of ytterbium silicide by furnace or rapid thermal annealing (RTA) at different temperatures e.g.: 300-360 °C [1], 450 °C [4], 530 °C [5], 600 °C [3], and 200-800 °C [6].

Among many ytterbium silicides (e.g. Yb₂Si, Yb₅Si₃, Yb₅Si₄, YbSi, Yb₃Si₄ and Yb₃Si₅) the most known is the YbSi_{2-x} phase [7-8]. Its structural properties are very similar to the well known ErSi_{2-x} phase [9]. The maximum silicon content in YbSi_{2-x} was established to be equal to 63.5 atomic % of Si [8]. The value of 63.5 atomic % Si is close to the YbSi_{1.8} formula and it is a silicon-rich ytterbium silicide phase, which crystallizes with the hexagonal AlB₂ type. Ytterbium silicide and other RE

silicides with the hexagonal AlB_2 crystal structure have an excellent lattice match with silicon, so that high quality silicide thin films can be grown on silicon [9].

2. Experimental

The 20 nm thick ytterbium film was deposited by e-gun evaporation on the silicon substrate. One hour annealing of the Yb/Si structure at 480 °C has been applied to form ytterbium silicide. RE metals are known to react with oxygen. In order to omit applying a capping layer, the formation of ytterbium silicide was performed under special conditions, which also protect well against oxidation. For this reason, the annealing of the studied Yb/Si structure was carried out under ultra-high vacuum (UHV) conditions, without breaking the vacuum between deposition and annealing. For the investigation of the mechanisms of the ytterbium silicide formation in the Yb-Si/Si structure, transmission electron microscopy (TEM) specimens were prepared by the conventional cross-section method using low-temperature argon ion milling. TEM studies were focused on microstructural observations of silicide layers and silicide/Si interfaces at an atomic scale by HRTEM (JEOL-4000FX), as well as on the identification of formed silicide phase using EDS in scanning TEM (VG HB501UX, with the electron beam size diameter of 0.7 nm, as determined by the full width at half maximum (FWHM)). A non-annealed sample was also investigated for comparison.

3. Results and discussion

The HRTEM image presented in Fig. 1a clearly shows that during the deposition of the Yb-layer on the silicon substrate, the reaction of ytterbium with silicon took place. As a result a 5 nm thick amorphous silicide layer was formed at the Yb/Si interface. This layer has very flat interfaces with the Yb-layer and the silicon substrate, respectively. The thickness of the Yb-layer after deposition is 15 nm. It means that about 25% of the Yb-layer reacted with silicon during the deposition process. The Yb-layer consists of columnar grains. The formation of an amorphous interlayer between the metal and the substrate just after metal deposition on silicon was already proved in many metal/silicon systems [10]. The growth of the amorphous phase stops when the critical thickness, usually several nanometers, is reached.

Figure 1b presents an image of the Yb/Si structure annealed at 480 °C for one hour. During annealing at this temperature, the entire Yb-layer reacted with silicon, forming a silicide layer that consists of two phases, in the form of continuous layers. The bottom layer is crystalline and the upper one is amorphous. The total thickness of both layers is about 18-20 nm and the thicknesses of the crystalline and amorphous parts constitute 2/3 and 1/3 of the whole thickness, respectively. The top surface and all interfaces in the annealed sample are rough. The phase at the bottom, i.e the crystalline layer, was identified by EDS as the YbSi_2 phase (Fig. 2a). Although the EDS measurements showed that the ratio of atomic concentration of ytterbium and silicon in crystalline silicide is about 1:2 or more, however the crystalline silicide phase probably corresponds to the Si-rich $\text{YbSi}_{(-1.8)}$ phase [7-8]. The small differences in EDS measurements result from the sputtering of the material from the Si substrate caused by the ion milling process.

According to the equilibrium phase diagram for Si-Yb, obtained experimentally using furnace annealing, the Si-rich YbSi_{2-x} phase is not expected to form below 770 °C [7-8]. However, many other detailed studies (for both, furnace and RTA annealing) showed that this phase is formed already at significantly lower temperatures [1,3-6,11], sometimes even at 300 °C. It brings the conclusion that although the Yb-Si systems have already been studied by some research groups, the kinetics involved in the interface formation of ytterbium silicides or others RE silicides is still poorly understood [7].

It was reported that RE disilicides can crystallize with three closely related types of crystallographic structure: ThSi_2 , GdSi_2 and AlB_2 [8]. GdSi_2 can be considered as an orthorhombic deformation of the tetragonal ThSi_2 type and the most frequent hexagonal AlB_2 type is a representative of a transposition structure of ThSi_2 .

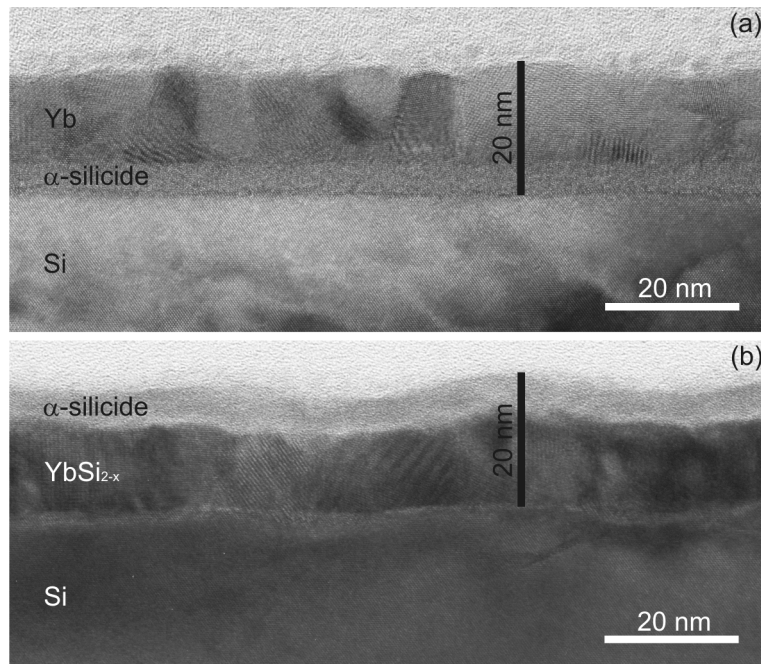


Figure 1. HRTEM images of (a) an as-deposited Yb/Si structure and (b) structure annealed at 480 °C for one hour.

The HRTEM image presented in Fig. 2b reveals a very distinct silicide/silicon interface, as well as differences in lattice parameters between silicide and silicon. An arrangement of ytterbium silicide atoms visible in the HRTEM image does not correspond to the YbSi_{2-x} phase with the hexagonal AlB_2 type structure. Probably, the YbSi_{2-x} phase formed in our sample after annealing at 480 °C corresponds to either ThSi_2 or GdSi_2 types of structures.

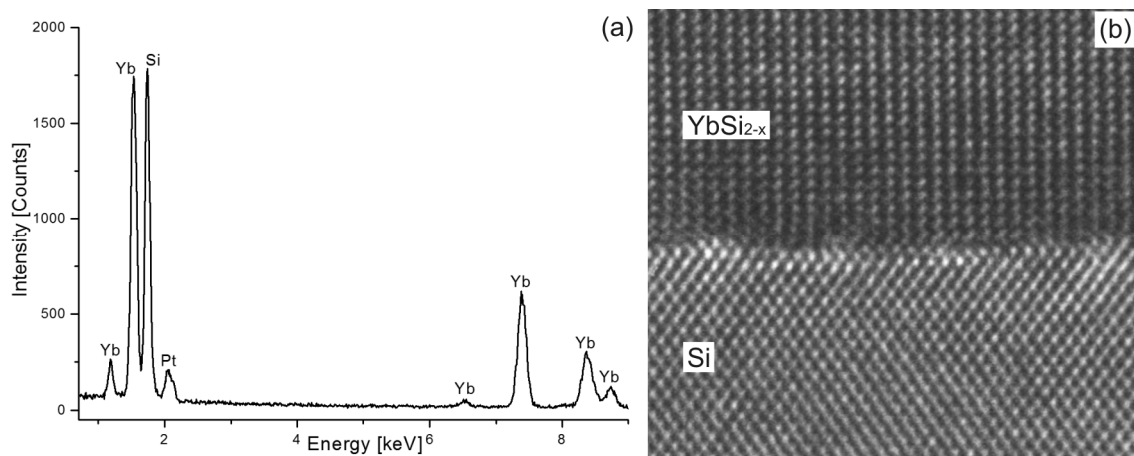


Figure 2. The Yb/Si structure annealed at 480 °C for one hour: (a) EDS spectrum obtained from the crystalline silicide layer and corresponding to the YbSi_{2-x} phase, and (b) HRTEM image of the silicide/silicon interface.

EDS measurements showed that atomic concentrations of ytterbium and silicon in the amorphous silicide layer, which was formed above the crystalline layer, are similar to results obtained for the crystalline YbSi_{2-x} layer. The formation of the amorphous phase above the crystalline phase in our annealed sample can be explained by the following hypothesis. In the first step of the solid-state

reaction, a thin amorphous silicide layer forms at the Yb/Si interface, and then the amorphous phase moves up to the surface, consuming the Yb-layer. Then a crystalline phase nucleates at the α -silicide/Si interface and consumes the amorphous phase moving up to the surface. However, in our case the crystalline phase grew up to 2/3 of the silicide layer thickness. In this case the conditions of the process were insufficient to form a crystalline structure in the entire thickness of the silicide layer. This effect should be taken into account during optimization of annealing conditions.

4. Conclusions

The formation of ytterbium silicide fabricated by annealing at 480 °C has been studied by means of advanced TEM techniques. The formation of an amorphous silicide layer between the Yb-layer and the silicon substrate was already observed in the as-deposited sample. Annealing of the Yb/Si structure at 480 °C forms ytterbium silicide. However, ytterbium silicide consists of two different layers: a thicker crystalline layer and a thinner amorphous one. The phase formed in the crystalline layer corresponds to YbSi_{2-x} . However the observed crystal structure is different from the hexagonal AlB_2 type that is the most frequently observed for RE disilicides.

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