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# Transmission electron microscopy study of erbium silicide formation from Ti/Er stack for Schottky contact applications

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**Key words.** Erbium silicide, transmission electron microscopy.

## Summary

In this paper, we present results of transmission electron microscopy studies on erbium silicide structures fabricated under various thermal conditions. A titanium cap has been used as a protective layer against oxidation during rapid thermal annealing of an erbium layer in a temperature range of 300–700°C. Both layers (200 nm Ti and 25 nm Er) were deposited by electron-beam sputtering. The investigations have shown that the transformation of the 25-nm-thick erbium into erbium silicide is completed after annealing at 500°C. At higher temperatures, the formation of a titanium silicide layer above erbium silicide is observed. The lowest Schottky barrier has been measured in the sample annealed at 700°C.

## Introduction

Due to the relatively low Schottky barrier height (SBH) to *n*-type silicon, erbium silicide is a very attractive material for an application as a source/drain in *n*-channel Schottky Barrier MOSFET devices. Several methods, such as epitaxial growth (Knapp & Picraux, 1986), ion beam implantation (Wu *et al.*, 1996) and co-evaporation of the Si and Er (Frangis *et al.*, 1996) have been applied to synthesise erbium silicide. However, the most commonly used method of obtaining erbium silicide films is a solid-state reaction between an Er layer and a Si substrate (e.g. Baglin *et al.*, 1980). This reaction occurs during annealing at temperatures in the range of 400–700°C. Erbium as a rare earth (RE) element is very sensitive to oxygen contamination, which easily occurs even

when Er is temporarily subjected to air. Annealing of oxygen-contaminated Er results in poor quality erbium silicide layers. The best way to avoid this is to carry out both steps – Er layer deposition and subsequent annealing – under the same Ultra High Vacuum (UHV) conditions in a reactor that enables subsequent deposition and annealing without breaking the vacuum. In case of using conventional evaporation-annealing systems, when the vacuum has to be broken, the Er layer is protected against oxygen contamination by use of a capping layer. There are reports of the application of Pt/W (Tu *et al.*, 1981) or Pt/Si (Janega *et al.*, 1989) systems as a protecting cap. Very promising results were obtained by using a Pt layer over Er (Tang *et al.*, 2003), where a Schottky barrier lower than 0.1 eV has been obtained after 2 min rapid thermal annealing (RTA) at 600°C. However, the use of Pt is not a good solution taking into account further device integration processes. Pt is soluble only in aqua regia, which removes also erbium silicide. This makes Pt very difficult to be applied in silicide-based SB MOSFET devices, although the problem of Pt wet selective etching is going to be solved (Breil *et al.*, 2007).

In this paper, we present results of TEM characterisation of erbium silicide formation with Ti as a protective capping layer. Titanium is a promising metal for such application since it is selectively etched against erbium silicide with a sulphur peroxide mixture (SPM). Titanium has been already used as a capping layer during the silicidation of Er on SiGe (Yiew *et al.*, 2006) and for fabrication of erbium germanide on Ge (Liew *et al.*, 2006). The use of Ti-based (TiN) protective capping layers during the fabrication of ErSi<sub>2-x</sub>-based Schottky diodes has also been reported (Tan *et al.*, 2006).

## Experimental

The starting wafers were low-doped *n*-Si (100) bulk wafers (phosphorus-doped with a resistivity of 5–10 Ω cm). The Si

wafers were cleaned in SPM (50% H<sub>2</sub>SO<sub>4</sub> + 50% H<sub>2</sub>O<sub>2</sub>) for 10 min, rinsed in de-ionized water for 10 min, and dried by spinning under N<sub>2</sub>.

Then, the wafers were dipped into 1% hydrofluoric (HF) acid to remove SiO<sub>2</sub> grown during the SPM cleaning, rinsed and dried as previously mentioned. The samples were then introduced into the evaporator immediately after the preparation steps, in order to limit the oxide regrowth as much as possible. Erbium (25 nm) and titanium (200 nm) layers were deposited consecutively by e-beam evaporation on low-doped ( $1 \times 10^{15} \text{ cm}^{-3}$ ) *n*-type silicon substrates. The substrates were not heated during evaporation. The erbium silicide was formed by solid-state reaction between the Er layer and the Si substrate during an RTA process for 2 min at temperatures between 300°C and 700°C. For the investigation of the mechanisms of the erbium silicide formation in the Ti/Er/Si structure, TEM specimens were prepared by the conventional cross-section method. The studies were focused on the observations of the layer microstructure by TEM (JEOL 200CX) and of Er/ErSi/Si interfaces at the atomic scale by high-resolution transmission electron microscopy (HRTEM-JEOL-4000FX). The EDS spectra were taken by the EDAX spectrometer mounted in Philips CM 200 microscope working with 30 nm beam diameter.

## Results and discussion

In Fig. 1, TEM images of the initial stack with a 200 nm thick Ti protective layer are shown – an overall image in Fig. 1(a) and the HRTEM image of the Er/Si interface in Fig. 1(b). Considering the behaviour of such a system during thermal processing, it should be taken into account that during evaporation of the Er layer in UHV conditions an intermixing of Er and Si atoms occurs, resulting in the existence of a thin amorphous layer just after metal deposition (Luo & Chen, 1997). Such approximately 5-nm-thick layer is visible in Fig. 1(b). Figure 2 shows the structure of the erbium silicide layers after annealing at various temperatures: 300°C (Fig. 2(a)), 400°C (Fig. 2(b)), 500°C (Fig. 2(c)), 600°C (Fig. 2(d)) and 700°C (Fig. 2(e)). The initial amorphous layer formed during metal deposition slightly increases its thickness (to approximately 10 nm) after annealing at 300°C. The erbium silicide layer obtained after annealing at 400°C consists of a polycrystalline sublayer at the bottom part and an amorphous sublayer at the upper part. These two sublayers, with locally very different thickness ratios, give in summary 25-nm-thick erbium silicide layer. After annealing at 500°C, the entire 25-nm-thick silicide layer is polycrystalline. However, above the silicide layer the 10-nm-thick amorphous layer is present. In the sample annealed at 600°C, a thin (15 nm thick) additional polycrystalline layer is visible between erbium silicide and Ti. After annealing at 700°C, a 30-nm-thick very well defined polycrystalline erbium

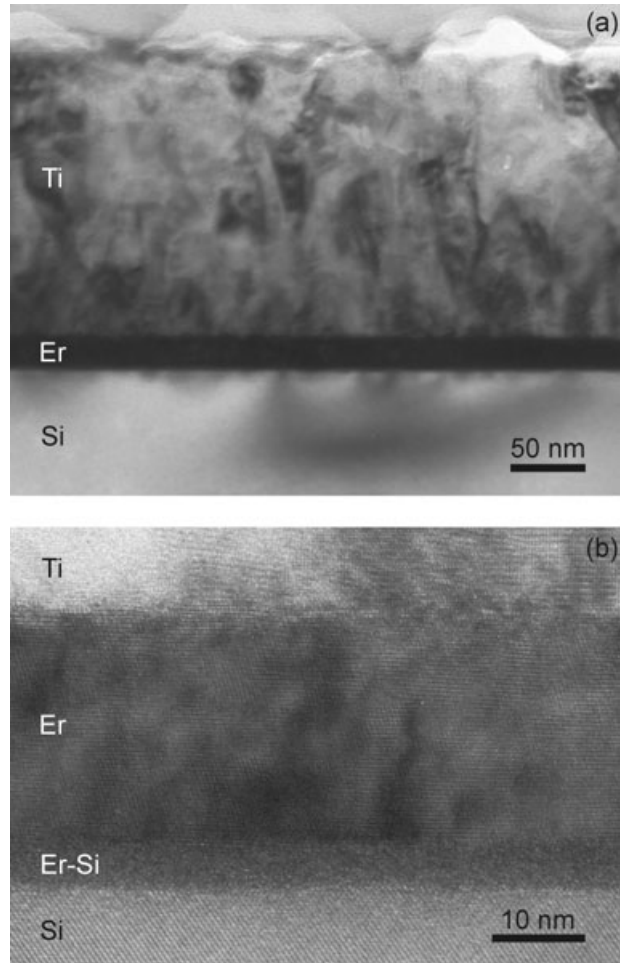


Fig. 1. The TEM cross-section of the (200 nm)Ti/(25 nm)Er stack after deposition: (a) overall view, (b) high magnification image of Er-Si interface.

silicide layer with sharp, but slightly undulated interfaces, has been obtained. Any intermediate layer is no longer visible at these interfaces.

In an Er-Si system, the mobility of silicon atoms plays a dominant role (Baglin *et al.*, 1981). Their diffusion during a heating process makes the solid-state reaction possible. As we can conclude from the TEM micrographs, during annealing at 300°C this diffusion is not very fast. A small amount of Si atoms reaches the Er/Si interface increasing only the thickness of the amorphous intermediate layer. However, during annealing at 400°C Si atoms penetrate already the entire Er layer. Their concentration at the bottom part is enough to form crystalline erbium silicide (ErSi<sub>2-x</sub>) which is visible in Fig. 2(b). The concentration of Si atoms at the upper part of the layer is still too low to form a crystalline structure and only an amorphous phase is observed. The formation of the ErSi<sub>2-x</sub> crystalline phase at the silicide/silicon interface has been observed, e.g. in furnace annealed erbium layers on silicon at 270°C (Luo & Chen, 1997). The existence of such phase has

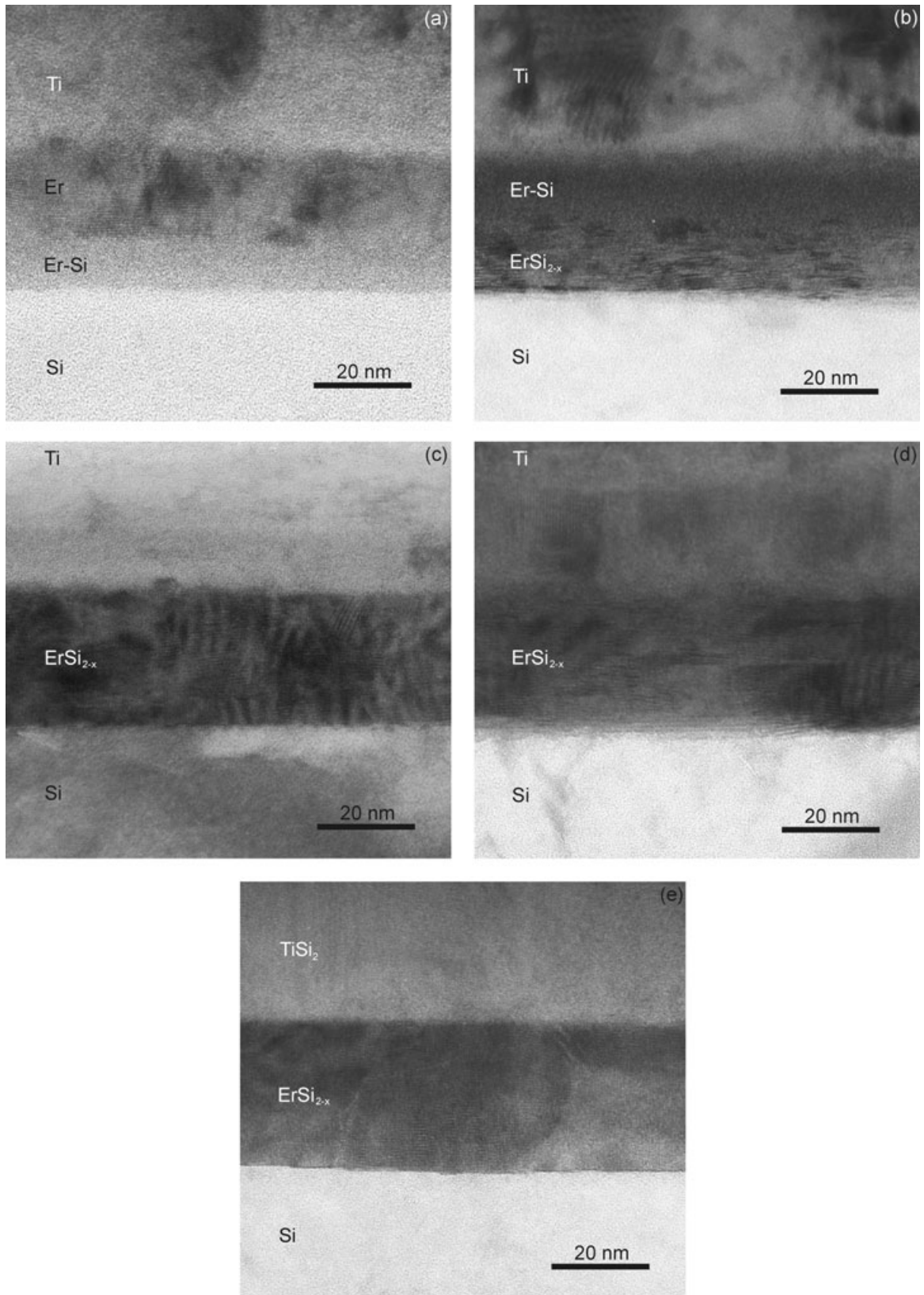


Fig. 2. The structure of the Ti/Er/Si layers after RTA (2 min) annealing at: (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C.

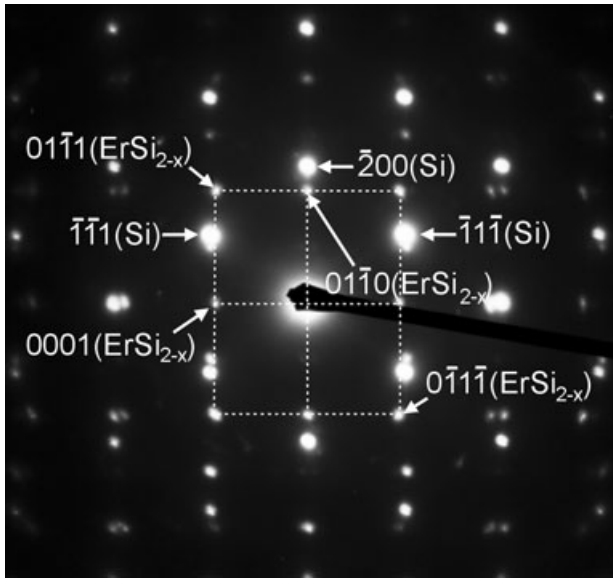


Fig. 3. Electron diffraction pattern with marked [011]-orientated Si reflections and  $[2\bar{1}\bar{1}0]$ -orientated reflections corresponding to the hexagonal  $\text{ErSi}_{2-x}$  phase.

been also confirmed by the authors (Reckinger *et al.*, 2008) in the erbium silicide formed by RTA under a 10-nm-thick Ti cap with the use of X-rays diffraction (XRD). However, in the present investigations XRD could not be used due to high signal screening by the relatively thick (200 nm) titanium layer. After annealing at 400°C and at higher temperatures the Er layer is no longer observed. In Figs 2(c) and (d) (500°C and 600°C, respectively), the fully crystallized  $\text{ErSi}_{2-x}$  layers are visible. The formation of this phase has been confirmed by the analysis of the diffraction pattern at 600°C where diffraction spots corresponding to the hexagonal  $\text{ErSi}_{2-x}$  structure are present (Fig. 3). The amorphous layer of unknown composition formed above  $\text{ErSi}_{2-x}$  at 500°C is not observed after annealing at 600°C. Since the thickness of the layers formed at 500°C and at 600°C is very similar (about 25 nm) one can conclude that this layer is not uncrystallized erbium silicide but rather titanium highly saturated with silicon atoms (Ti–Si mixture).

In the paper of Reckinger *et al.*, the erbium silicide layers obtained under thin 10-nm cap were divided for two sublayers. The composition of the lower sublayers has been determined as the pure  $\text{ErSi}_{2-x}$ . The upper layers were formed as a silicide highly contaminated with oxygen. In contrary to these observations in the results presented here (Fig. 2(c–e)), such division is not visible. The layers are homogeneous at over the whole thickness. It shows that the thick titanium cap well protects Er layer against oxygen penetration.

The thickness of the  $\text{ErSi}_{2-x}$  layer formed at 700°C is slightly larger than obtained at lower temperatures. The differences seem to occur due to difference between the orientation of grains formed at 700°C and in lower temperatures. The layer formed at 700°C consists of large grains oriented in the same

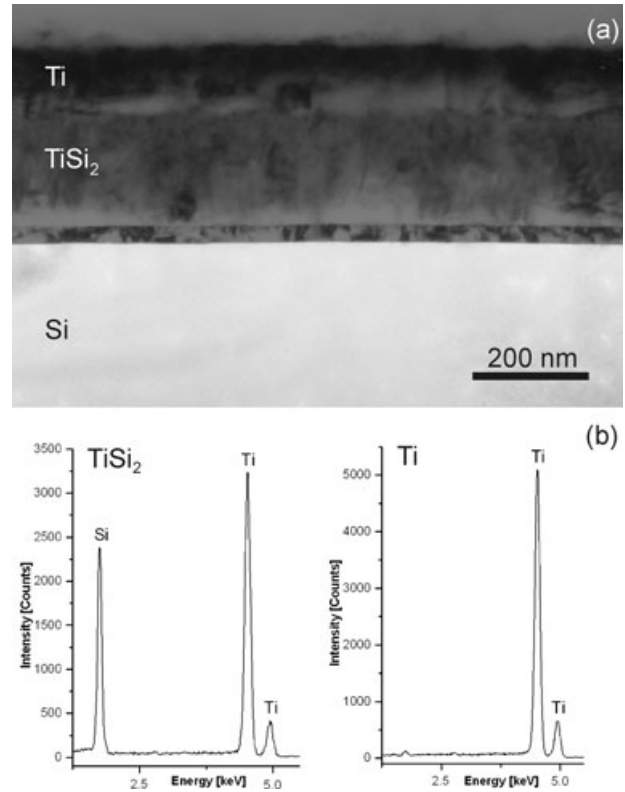


Fig. 4. (a) The structure of the Ti/  $\text{ErSi}_{2-x}$  layers after RTA (2 min) annealing at 700°C (b) EDS spectra of the Ti and  $\text{TiSi}_2$  layers.

direction. This structure is less condensed in comparison with structures formed at lower temperatures (500°C and 600°C) where smaller grains oriented in different directions were observed.

The TEM image of the overall sample annealed at 700°C is presented in Fig. 4(a). Two layers are visible above the  $\text{ErSi}_{2-x}$ . The first one located directly on silicide is approximately 200 nm thick and the second one, the top layer of the structure, is 125 nm thick. Energy dispersive X-ray spectroscopy measurements (Fig. 4(b)) have shown that the first layer consists of Ti and Si atoms and the second layer consists of pure Ti. The concentration of Si atoms (quantified using standardless ZAF method) in the bottom layer is nearly two times larger than the concentration of Ti atoms. This may suggest that another layer of a silicide phase, namely titanium silicide with a composition corresponding to the commonly known titanium silicide,  $\text{TiSi}_2$ , phase has been created above the erbium silicide.

This phase is presumably formed due to high Si diffusion through the erbium silicide layer at high temperature. The ratio of the newly formed titanium silicide layer thickness (200 nm) to the thickness of consumed part of titanium layer (75 nm) is equal to 2.7. It is in agreement with data published in the literature where, e.g. Rutherford backscattering (RBS) measurements have shown that the ratio of the titanium

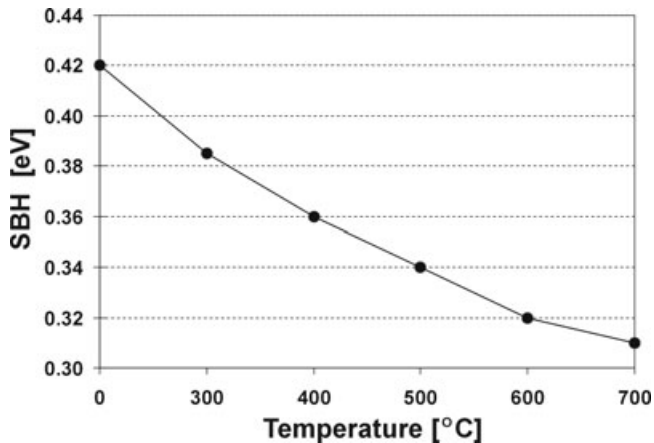


Fig. 5. Schottky barrier height dependence versus annealing temperature. The barrier heights were extracted using an activation-energy-based method (Dubois & Larrieu, 2004).

silicide thickness to the thickness of initial Ti layer may reach 3 depending on annealing temperature and time (Rèvész *et al.*, 1983). The silicidation of titanium begins at temperatures 475–550°C. (Bentini *et al.*, 1985). It is possible that in the analysed samples this process also started in this range and the amorphous and the polycrystalline layer observed above the silicide layer after annealing at 500°C and at 600°C, respectively, are titanium silicide layers.

The measurements of the SBH have shown that the barrier decreases with an increase of the annealing temperature (Fig. 5). The lowest barrier heights have been obtained after annealing in 600–700°C temperatures range. The barrier height measured after 700°C annealing (i.e. 0.31 eV) is 0.01 eV lower than that obtained after annealing at 600°C. This is in contrast to the Pt/Er/Si system (Tang *et al.*, 2003) where annealing at 700°C caused an increase of the barrier height due to the reaction of Pt with Er. In the Ti/Er system, the reaction between Ti and Er does not occur below 800°C (Thompson *et al.*, 1985) and has not been observed in our experiments. In spite of better anti-oxidation protection of the 200-nm-thick titanium layer, the lowest obtained SBH is higher than that measured in the silicide formed under thin (10 nm) Ti cap (Reckinger *et al.*, 2008). The temperature at which the lowest SBH was obtained in samples where the 200-nm-thick Ti cap was used was also almost 200°C higher than that obtained for samples with the thinner (10 nm) Ti cap.

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