Transmission electron microscopy (TEM) characterisation of Ru_2Si_3 thin films formed by solid state reaction of Ru and Si

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Introduction

Semiconducting silicides Ru_2Si_3 have received considerable attention in recent years due to its direct band gap and it potential application for infrared light emitting diodes at 1.5 micron metre wavelength, which corresponds to the absorption minimum in optical glass fibres. Recently, the compatibility of Ru_2Si_3 with Si has been demonstrated. In this study, thin films of Ru were sputtered on silicon substrate. Ru_2Si_3 films were formed by solid state reaction between deposited Ru and Si through post-annealing.

Experimental

A cross-sectional TEM sample was prepared by the usual method that involved grinding and polishing until its thickness was less than 10 microns. Ion milling was performed using Gatan PIPS Ion miller. Transmission electron microscopy (TEM) was performed using a JEOL JEM 2010F (JEOL, Japan) equipped with a field emission gun (FEG) operated at 200kV. The TEM was equipped with an energy dispersive x-ray (EDX) spectrometer and NORAN System SIX microanalysis system (Thermo Electron Corporation, USA) and GIF 2001 electron energy filter (Gatan, USA). All oxygen maps were collected using the O-K edge at 532eV energy loss together with the default setting in the DigitalMicrograph software. The energy selecting slit was 30eV wide and the three images used to create the maps were centred at: post-edge = 547eV, pre-edge 1 = 484eV and pre-edge 2 = 514eV.

Results

The bright-field TEM image in Fig. 1(a) shows that the film is about 80 nm thick and is composed of columnar grains 20 nm across. A layer of 5 – 7 nm thick was found on top of the film and an interlayer of 5 – 7 nm was found between the film and the silicon substrate. A thin bright line between the interlayer and Ru_2Si_3 film indicates a region of porosity.

EELS elemental mapping was performed in order to study the distribution of elements in the film. Figure 1 (b) shows the EELS oxygen map acquired from the region shown in Fig. 1 (a). The spectrometer was configured to transmit only those electrons which had lost 532 eV due to the excitation of oxygen K-shell electrons in the specimen. The resulting image therefore represents the distribution of oxygen in the region imaged, with brighter areas indicating more oxygen. The resulting oxygen map is rather noisy due to low signal intensity and background correction procedures; however, it shows clearly that the top layer contains oxygen. The bright region in Figure 1(a) above the interlayer at the substrate interface also contains oxygen. Elemental jump ratio mapping provides an alternative technique for visualising the oxygen distribution. An image of 532 eV energy loss is divided by an image of slightly lower energy loss (below the oxygen ionisation energy). The resulting image, Figure 1 (c), clearly shows that the top layer consists of an oxygen rich layer and embedded nano-size clusters, which do not contain oxygen. One of the embedded clusters is marked both in the oxygen-jump image, Fig. 1 (c), and the bright-field image, Fig. 1(a).

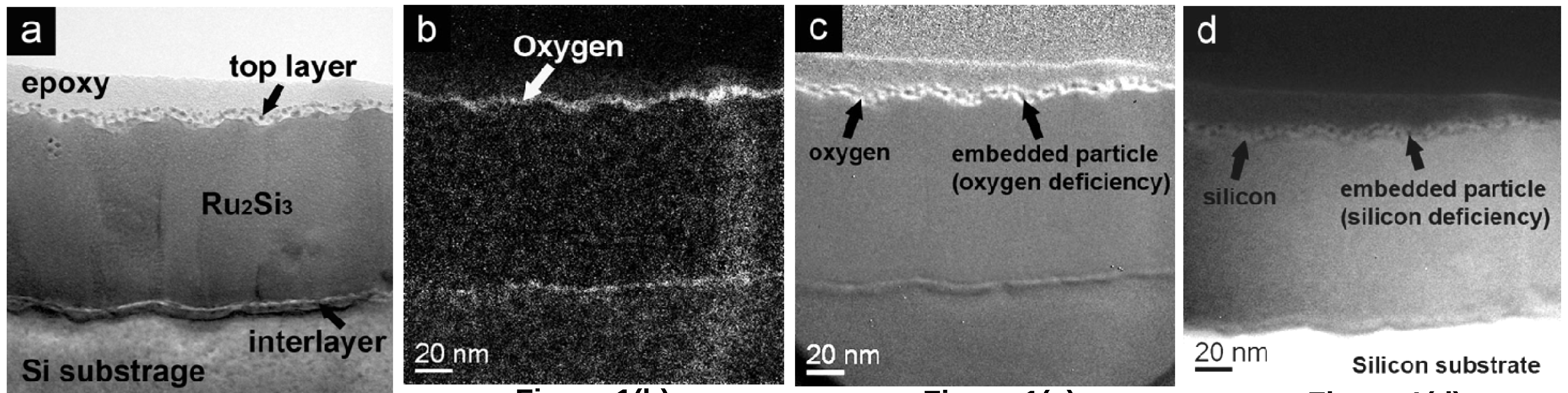

Figure 1(a) Figure 1(b) Figure 1(c) Figure 1(d)

The distribution of silicon is shown in the EELS map in Figure 1(d). Silicon is detected in the film which is consistent with a fully reacted Ru_2Si_3 film indicated by XRD results. More importantly, the top layer, which contains oxygen, also contains silicon. The clusters embedded in the layer, however, do not show any detectable silicon as indicated by the arrow. The oxygen-jump ratio map and silicon map therefore suggest that the top layer is SiO_2 with embedded Ru clusters in the layer. The interlayer between the film and substrate does not appear to be a single composition. It contains both silicon and oxygen as evidenced by Figures 1(d) and (b), respectively, but there also appears to be a deficiency of Si at the interface between the substrate and interlayer. This may be a residual Ru layer. Unfortunately, attempts at ruthenium EELS mapping were not successful. Energy dispersive x-ray mapping will be attempted.

Figure 2 shows the high resolution image of the top layer and the upper part of the film. Lattice fringes in the loosely attached nano grains are consistent with the spacing of Ru planes. The HRTEM images support the results from the EELS element mapping; the top layer of the film is composed of 2 – 4 nm nano clusters of Ru embedded in a 7 nm thick SiO_2.

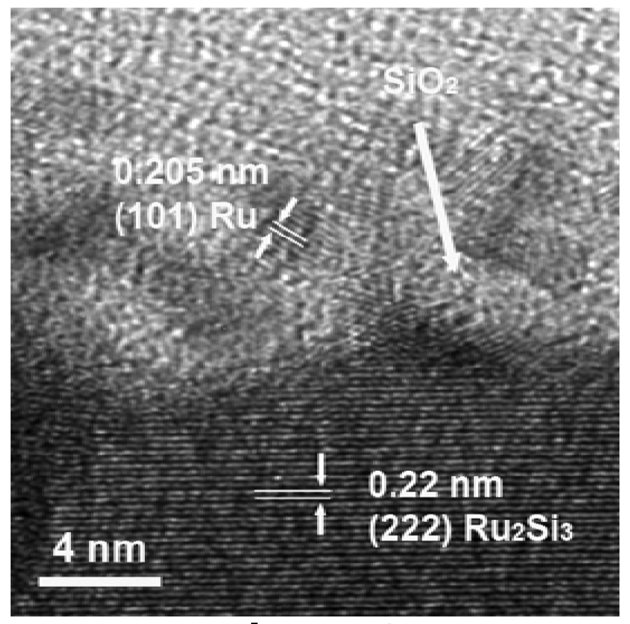

Figure 2

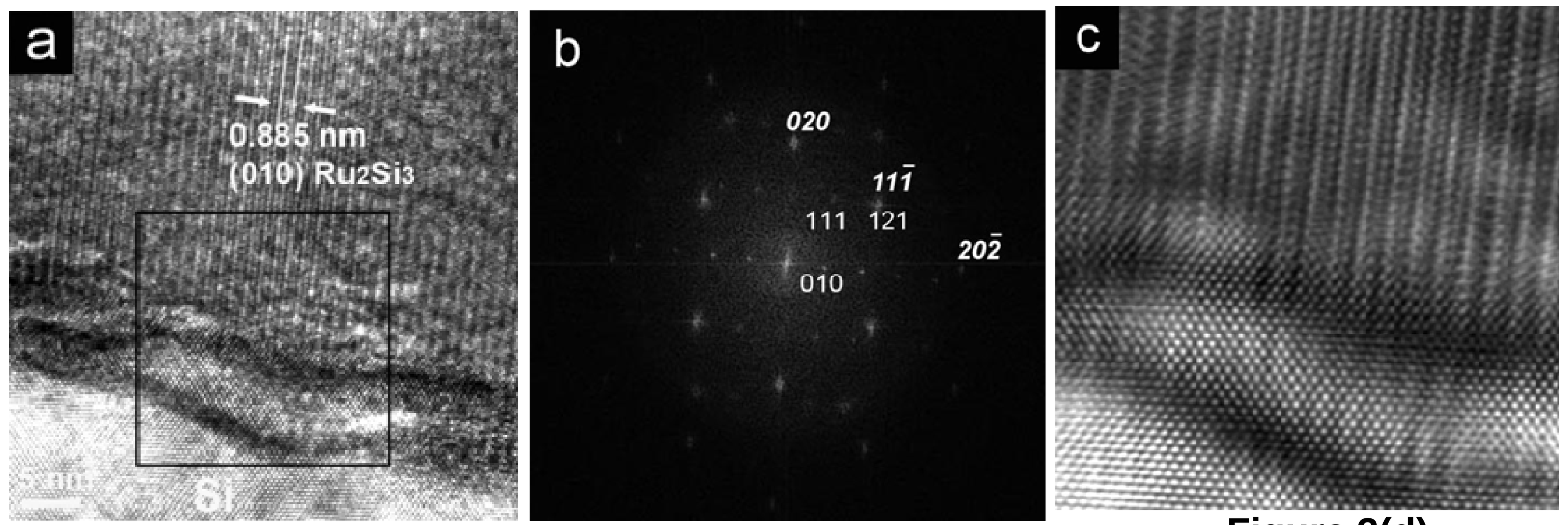

Figure 3(a) Figure 3(b) Figure 3(d)

The interface between the Si substrate and the Ru_2Si_3 film was studied by HRTEM. In Fig. 3(a) the interface region is marked by a square. The power spectrum of Fast Fourier Transformation is shown in Fig. 3(b). The two sets of spots associated with lattice planes from Si and Ru_2Si_3 are clearly discernable. The planes corresponding to silicon substrate are labelled with bold italic font. Using the published lattice constants for Ru_2Si_3: a = 1.1057 nm, b = 0.8934 nm, c = 0.5533 nm (*D.J. Poutcharovsky, E. Parthé, Acta Crystallogr. B 30 (1974) 2692 – 2696.*), the (010), (111) and (121) planes are identified and labelled. Using silicon as the calibration, the interplanar distances of the following planes were measured on the HRTEM image as: d_{010} = 0.885 nm and d_{111} = 0.418 nm. They are 1% and 3% less than the values obtained from the lattice constants of Ru_2Si_3, which give d_{010} = 0.8934 nm and d_{111} = 0.4329 nm. The (010) plane of Ru_2Si_3 is 4.7 tilted from plane of Si and it means that (101) plane of Ru_2Si_3 is also 4.7 tilted from (010) plane of silicon, which is the plane for the growth of Ru and Ru_2Si_3 grains. The FFT power spectrum also shows that (121) plane of Ru_2Si_3 is coincident with of Si. The orientation relationship between the Ru_2Si_3 grain and the Si substrate can be described as follows: Ru_2Si_3(101)//Si(001) and Ru_2Si_3[010]//Si with 4.7 mismatched. It should be noted that other orientation relationships were also observed. The filtered high magnification image of the marked region, in Fig. 3(c) shows an important observation; the silicon fringes run into the interlayer between the substrate and the film. The interlayer therefore has the same structure as silicon.

Conclusion

In summary, the sputtered ruthenium film reacts with silicon completely and forms Ru_2Si_3 film after annealing at 700C in nitrogen for 5 minutes. The Ru_2Si_3 film is about 80 nm thick and is composed of 20 nm width columns of Ru_2Si_3 grains. A top layer of SiO_2 with embedded Ru clusters, which is about 7 nm thick, was observed. We attribute the formation of the top layer to the oxidation between residual oxygen traces in the nitrogen and the silicon in Ru_2Si_3 grains. The observation is in agreement with electrical measurements by Jelenkovic et al. (*E.V. Jelenkovic, K.Y. Tong, W.Y. Cheung and S.P. Wong, Semicond. Sci. Technol. 18 (2003) 454 – 459*) After the reaction of Ru_2Si_3 with oxygen and the formation of SiO_2, Ru clusters are left in the top layer as evident by TEM elemental mapping and HRTEM images. The interlayer between the film and substrate contains silicon and oxygen as evident from EELS element mapping; however, the interlayer structure appears similar to silicon in the substrate as evident from HRTEM image.

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