Proceedings of APAC-SILICIDE 2010

AES and EELS study of desorption of magnesium silicide films on Si(111)

Konstantin N. Galkin\textsuperscript{a*}, Mahesh Kumar\textsuperscript{b}, S.M. Shivaprasad\textsuperscript{b,c}, Nikolay G. Galkin\textsuperscript{a}

\textsuperscript{a}Institute of Automation and Control Processes, FEB of RAS, Radio, 5, Vladivostok, 690041, Russia
\textsuperscript{b}Surface Physics and Nanostructures Group, National Physical Laboratory, Dr K.S. Krishnan Road, New Delhi, India
\textsuperscript{c}International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

Abstract

During AES and EELS investigations of thermal stability of Mg and Mg\textsubscript{2}Si films it was found that metallic Mg desorbs from the surface at temperatures higher than 80\textdegree{}C, but the bulk-like Mg\textsubscript{2}Si film shows a thermal stability up to 180\textdegree{}C. The maximal thermal stability up to 230\textdegree{}C was observed for a two-dimensional magnesium silicide with structure (\(\sqrt{3}\times\sqrt{3}\))\textsubscript{-R30°}. A model of its thermal stability based on the peculiarities of the electronic structure of a two-dimensional magnesium silicide with structure (\(\sqrt{3}\times\sqrt{3}\))\textsubscript{-R30°} and on the continuity of 2D film was proposed.

\(\odot\) 2010 Published by Elsevier B.V. Open access under \textit{CC BY-NC-ND license}.

Keywords: Mg; Mg\textsubscript{2}Si; two-dimensional films; temperatural stability; desorption

1. Introduction

Low-dimensional magnesium silicide (Mg\textsubscript{2}Si) in the form of islands, thin layers or buried structures is scientifically and technologically important material, especially for application in thermo-electrics, etc.

Formation of the ordered two-dimensional magnesium silicide with structure (\(\sqrt{3}\times\sqrt{3}\))\textsubscript{-R30°} [1] and nanosized islands of Mg\textsubscript{2}Si [2] on Si(111) has already been investigated. It is known [3] that magnesium silicide in ultra-high vacuum conditions quickly disintegrates at temperatures higher than 200\textdegree{}C following magnesium desorption. This fact complicates the use of molecular beam epitaxy at silicon growth atop magnesium silicide. The desorption process of magnesium silicide from the two-dimensional phase with structure (\(\sqrt{3}\times\sqrt{3}\))\textsubscript{-R30°} or islands was not investigated previously, however.

\* Corresponding author. Tel.: +7-4232-320-682; fax: +7-4232-310-452.
E-mail address: galkinkn@iacp.dvo.ru.
2. Experiments

The experiments were performed in situ in an ultra-high vacuum chamber equipped with surface characterisation probes such as Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS). The sample was cut (size 7x19x0.32 mm$^3$) from commercial p-type Si(111) wafers with a resistivity of $\rho=10\ \Omega\cdot\text{cm}$. The system details and the cleaning procedure are given elsewhere in [4]. The atomic cleanliness of the sample was further confirmed by the absence of any detectable oxygen and carbon peaks in the AES spectrum, which also resulted in the well-defined and ordered (7x7) LEED pattern of Si(111).

Four different films were prepared for investigation of desorption process: a film of metal magnesium (thickness 3 nm) and three different magnesium silicide films. The magnesium was evaporated ($v=0.4\ \text{nm/min}$) on the substrate with different substrate temperatures: 25, 150 and 200$^\circ\text{C}$ for the formation of three films. The film of metallic magnesium was formed at room temperature (25$^\circ\text{C}$); the growth of two-dimensional magnesium silicide with structure $(\frac{\sqrt{3}}{2}\times\frac{\sqrt{3}}{2})_{R30^\circ}$ was observed at 150$^\circ\text{C}$, but only three-dimensional islands of bulk-like magnesium silicide (3D islands Mg$_2\text{Si}$) were formed at 200$^\circ\text{C}$. For the formation of bulk-like Mg$_2\text{Si}$ film the magnesium was evaporated at the rate of $v=0.06\ \text{nm/min}$ on silicon substrate held at room temperature [5].

3. Results and Discussion

The changes in ratio of Mg and Si Auger-peaks (normalised Mg Auger-peaks) versus the temperature of isochronous (one minute) annealing for different grown samples are presented in Figure 1. Samples were annealed beyond the temperature of adsorption only. Values at 50$^\circ\text{C}$ correspond to initial film intensity. The regions of constant intensity of normalised magnesium Auger-peak and regions with sharp and smooth changes are observed for all films. The first regions correspond to stability of structure at the given temperatures whereas the second and third regions correspond to destruction of a structure. Difference in the two last regions results in various rates of destruction and desorption, and also, probably, in mechanisms of structure destruction. Thus Mg film is stable up to 80 $^\circ\text{C}$ and after this temperature a strong decrease in normalised magnesium Auger-peak intensity is observed. The two-dimensional Mg silicide film conserves stability up to 230$^\circ\text{C}$ and then it begins to break up. The behaviour of bulk-like magnesium silicide formed at room temperature differs from the listed samples. Mg Auger-peak intensity decreases from 65$^\circ\text{C}$ gradually, probably because of the presence of free magnesium atoms and their desorption from surface layer at temperatures of 65-120$^\circ\text{C}$ during isochronous annealing; further, there is some stabilisation up to 175$^\circ\text{C}$ at the expense of crystallisation of the magnesium silicide layer following its destruction and Mg desorption. The gradual reduction of normalised magnesium Auger-peak intensity for a sample with 3D bulk-like islands is observed in temperatures higher than 200$^\circ\text{C}$ that corresponds to the gradual destruction of magnesium silicide and follows magnesium desorption from the silicide island surface. Therefore, with AES data it is possible to identify two critical temperatures: 175-200$^\circ\text{C}$ and 230$^\circ\text{C}$ for magnesium silicide (bulk-like and islands) and two-dimensional magnesium silicide.

Information about phase compositions of different sample surfaces changing during step-type annealing can give EELS spectra (Figure 2). The evolution of EELS spectra at isochronous (one minute) annealing at different temperatures for bulk-like magnesium silicide film is presented in Figure 2a. The presence of only strong Mg silicide peaks (9.6 eV and 14.6 eV [5]) and interband transition at 4.5 eV is evidence of Mg$_2\text{Si}$ formation without break of silicide film and Si segregation. A small shoulder at 7.5 eV [5] testifies, however, to the presence of a small quantity of metallic magnesium islands on the silicide surface that correlates with the proposal from AES data (Figure 1). From the Figure 2a we see that after annealing at 100$^\circ\text{C}$ the additional contribution (at 7.5 eV) in surface plasmon disappears, which
corresponds to full desorption of metal magnesium islands from a sample. The constancy of EELS and AES spectra in a temperature range of 100-165°C corresponds to stability of silicide film in this temperature range. After annealing at 190°C the peak of surface plasmon is widened, and the peak of bulk plasmon is also widened and shifted to higher energy by EELS data. The reduction of intensity of normalised Mg Auger-peak is also observed by AES data (Figure 1). Both facts correspond to the beginning of the break-up of bulk-like magnesium silicide film, the appearance of a small uncovered area of Si surface and desorption of some of the magnesium atoms from the silicide island surface. A sharp reduction of intensity of magnesium Auger-peak (Figure 1) and peak intensity of magnesium silicide surface plasmon (9.6 eV, Figure 2a) is observed after annealing at a temperature of 250°C with the subsequent observation of 1x1 spots in the LEED patterns that correspond to an increase of clean Si surface area and conservation of its crystal structure after the break-up of the silicide film, destruction of Mg silicide island surface, desorption of Mg atoms and formation of 2D MgSi islands. When Mg silicide is formed from an Mg layer by isochronous (one minute) annealing (Figure 2b, 2c), the low-dimensional silicide (plasmons 9.6 eV and 13.6 eV [5]) is formed at 135°C after desorption of metallic Mg at 80-100°C and is conserved up to 180°C without a break in its surface. At higher temperatures of 190-200°C film breaks on islands, but electronic structure of low-dimensional

Fig. 2 Evolution of EELS spectra (Ep=150 eV) at isochronous annealing during one minute for: (a) bulk-like Mg2Si, (b-c) film of metal magnesium and (d) 2D Mg2Si with structure (ћҐ3×ћҐ3)-R30°.
(2D) Mg$_2$Si is preserved. The lower temperature required for destruction of magnesium silicide film (180°C) is caused by its greater deficiency and smaller thickness compared with bulk-like Mg$_2$Si film formed at room temperature and annealed at the same temperature range (Figure 2a). At higher annealing temperatures (up 230°C) the bulk plasmon (13.6 eV) disappears and interband transition at 4.6 eV appears, so we can say that islands have the 3D bulk-like Mg$_2$Si structure and can suggest that the sizes of magnesium silicide islands are so small that it is impossible to observe a bulk plasmon of 3D Mg$_2$Si. The intensities of AES and EELS peaks for initially formed bulk-like Mg$_2$Si film (Figure 2a) and for 2D Mg$_2$Si formed from Mg layer (Figure 2b, 2c) are identical after annealing at 275°C and higher temperature. This confirms that desorption processes from 2D Mg$_2$Si islands do not depend on the pathway it has been formed. Substrate annealing at 275°C and higher temperatures reduces the sizes of silicide islands, so that it is impossible to observe a surface plasmon.

The desorption curve for two-dimensional magnesium silicide film with a structure of (\(\frac{\sqrt{3}}{3\times\sqrt{3}}\))-R30° formed at reactive deposition epitaxy at 150°C is characterised by a plateau in the 145-230°C temperature range that corresponds to its stability in this temperature range. An annealing at 240°C results in reduction of intensity of bulk plasmon (Figure 2d) and normalised Mg Auger-peak (Figure 1). Weak (1x1) spots together with (\(\frac{\sqrt{3}}{3\times\sqrt{3}}\))-R30° spots are also observed on LEED patterns. This corresponds to the destruction of two-dimensional silicide with an evident area of clean surface on which (1x1) LEED spots are observed. The electronic structure of 2D Mg$_2$Si, details of which are presented in [6], is, however, conserved in the islands formed. Significant reduction of EELS intensity of bulk 2D silicide plasmon and the appearance of bulk silicon plasmon and only (1x1) spots on LEED pattern were observed after annealing at 265°C. An annealing at 295°C results in full disappearance of bulk magnesium silicide plasmon and formation of one interband transition at 4.3 eV that corresponds to transformation of a lattice from 2D Mg$_2$Si in bulk-like magnesium silicide. With a further increase of annealing temperature, as well as for a case of desorption of bulk-like magnesium silicide film, desorption of magnesium from bulk-like Mg$_2$Si islands occurs. Therefore, a thermal stability of 2D Mg$_2$Si can be explained by two factors: electronic structure with fixed Mg-Si bonds [6] and greater activation energy of desorption for continuous 2D Mg$_2$Si grains larger than the coherence length of the LEED analyser.

4. Conclusions

The thermal stability of various Mg and Mg$_2$Si films on Si(111) was investigated by AES and EELS data registered after different temperature annealings. It was determined that metal magnesium starts to desorb from a surface at temperatures higher than 80°C unlike the film of bulk-like magnesium silicide which starts to be destroyed at temperatures above 180°C. The film of two-dimensional magnesium silicide with structure (\(\frac{\sqrt{3}}{3\times\sqrt{3}}\))-R30° shows the maximal thermal stability. Its structure is conserved up to 230°C. It was found that during desorption processes the transformation of 2D Mg$_2$Si lattice to bulk-like silicide lattice occurs during the annealing of Mg film. The reasons for the thermal stability of 2D Mg$_2$Si are described in the more stable framework of its electronic structure with fixed Mg-Si bonds and 2D Mg$_2$Si film compared with 3D islands.

Acknowledgements

The work was supported by RFBR (grant No 09-08-92653-IND a) and joint DST-RFBR project. One of the authors (K.N. Galkin) thanks to Prof. V.V. Korobtsov (IACP FEB RAS) and Dr. Govind (NPL, India) for fruitful discussions.

References