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Growth, stability and decomposition of Mg$_2$Si ultra-thin films on Si (100)

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Highlights

- An original growth of Mg$_2$Si ultra-thin silicide films is reported
- Growth mechanisms, stability, and decomposition processes of such nanometric silicide thin films are described.
- Decomposition of the Mg$_2$Si silicide under O$_2$ atmosphere through the formation of a stable MgO thin film is also reported.

ABSTRACT: Using Auger Electron Spectroscopy (AES), Scanning Tunneling Microscopy/Spectroscopy (STM/STS) and Low Energy Electron Diffraction (LEED), we report an in-situ study of amorphous magnesium silicide (Mg$_2$Si) ultra-thin films grown by thermally enhanced solid-phase reaction of few Mg monolayers deposited at room temperature (RT) on a Si(100) surface. Silicidation of magnesium films can be achieved in the nanometric thickness range with high chemical purity and a high thermal stability after annealing at 150°C, before reaching a regime of magnesium desorption for temperatures higher than 350°C. The thermally enhanced reaction of one Mg monolayer (ML) results in the appearance of Mg$_2$Si nanometric crystallites leaving the silicon surface partially uncovered. For thicker Mg deposition
nevertheless, continuous 2D silicide films are formed with a volcano shape surface topography characteristic up to 4 Mg MLs.

Due to high reactivity between magnesium and oxygen species, the thermal oxidation process in which a thin Mg$_2$Si film is fully decomposed (0.75 eV band gap) into a magnesium oxide layer (6-8 eV band gap) is also reported.

Keywords: Silicide, STM, Thin films, Surface, oxide

1. Introduction

Addressing the challenge of metal silicides integration into micro and nanoelectronics devices overlaps with several important and pressing requirements relying on exquisite control of their synthesis process. Therefore, epitaxial growth of metal silicides[1] has been extensively studied over the past few years, the main goals being to reach low contact resistances, a high thermal stability and a thickness control for films at a nanometric scale[2–7].

Magnesium silicide thin films, among others, have attracted much interest as promising indirect-gap semiconductors to be used in various electronic, mechanical and infrared optoelectronics applications. More recently, Mg$_2$Si ultra-thin films formed on silicon have shown great potential regarding both thermoelectric considerations and Si-based devices compatibility. By reducing the thermal conductivity provided by phonons, such low-dimensionality films would produce a pathway towards thermoelectric generators with high conversion efficiency[8]. The confined growth of nanometric thin films of Mg$_2$Si on silicon, however, has been stated as a challenging task. Mainly due to a sticking coefficient of Mg on Si that drastically decreases as the substrate temperature is raised (down to zero at 200°C with no more Mg condensation[9]), only a few groups have reported the successful formation of magnesium silicide thin films[10] or features [11] by reactive adsorption of magnesium on silicon substrates held at moderate temperatures.

In order to limit desorption while accessing a wider range of processing temperatures, thermal codeposition of Mg with Si has also been explored, namely on hot Si(100)[12] and Si(111)[10] substrates held at 200°C. Implying potential crossover reactions between the codeposited species and the Si surface atoms, codeposition was mainly used for growing thicker magnesium silicide films ranging from tens to hundreds of nanometers, where no accurate control of the thickness was expressly needed.

By growing thick oxide films on top of a deposited metal Mg layer or Mg$_2$Si film, encapsulation has finally been explored as a manner of limiting magnesium desorption during the annealing procedure. This method, while effective for promoting crystalline Mg$_2$Si formation by reactive diffusion at relatively low temperatures[13] [14] was shown to induce intermixing between the silicide and the encapsulating layer beyond 400°C [9].

In a previous work, our group has studied the spontaneous and self-limited formation of an ultra-thin Mg$_2$Si layer (70 pm thick) in the early stages of Mg deposition (0.25 ML) on
Ag(111)[15] and Si(100) at RT[1]. Used as a growth template for MgO atomic films, we have then reported the RT crystallization of this interfacial Mg$_2$Si driven by its partial decomposition under oxygen exposure[16]. With a similar approach here, we report in this study the formation of thin magnesium silicide films achieved by thermally enhanced solid-phase reaction of few Mg atomic monolayers on Si(100). Post-annealing treatment of Mg films of different thicknesses deposited at RT promotes silicidation reaction with both no magnesium desorption beyond 200°C and an accurate control of the thin silicides thickness. Thermal oxidation process performed at very low oxygen pressure allows following dynamically the kinetic-dependence of the Mg$_2$Si decomposition mechanism, together with its impact on the underlying silicon substrate.

2. Experimental details

All experiments were performed in-situ in an ultra-high vacuum (UHV) chamber housing Molecular Beam Epitaxy (MBE) growth facilities and surface-sensitive analysis technics, i.e. Riber CMA AES, Omicron Spectra LEED and Omicron Variable Temperature-STM/STS. The Si(100) single crystal was first outgassed at 700°C overnight and cleaned by repeated cycles of annealing at 1100°C prior to deposition. Mg$_2$Si thin film samples of various thicknesses were achieved using the following two-steps procedure. Magnesium thin films ranging between 0.3 nm and 2 nm thick (i.e. between 1 ML and 8 MLs) were firstly deposited on Si(100) at RT, from a calibrated effusion cell with a background pressure of 2 x 10$^{-10}$ Torr. The Mg$_2$Si thin films were then obtained by silicidation, through a solid-phase reaction between Mg and Si that was thermally enhanced under UHV by annealing the samples at 200°C for a few minutes. Note that the magnesium deposition rate was defined using coupled AES and STM calibrations stated in a previous work[1]. The AES plots were obtained in the derivative mode by monitoring the Auger intensities or peak-to-peak intensities of the following low-energy transitions: Si(LMM)$_{92}$eV, O(KLL)$_{511}$eV, Mg(LVV)$_{45}$eV, oxidized Mg(LVV)$_{35}$eV and silicide Mg(LVV)$_{43.5}$eV [17].

3. Results and discussion

Figure 1. (A) displays AES spectra recorded for the bare (100)-silicon surface and for a thin Mg$_2$Si layer that was formed by thermally enhanced solid-phase reaction, after 200°C annealing of 8 Mg monolayers (thickness of about 2 nm) deposited on the substrate. Please note that Mg deposition process was always performed at RT, before promoting the silicidation with a thermal treatment under UHV environment. The first spectrum shows a single Si$_{92}$eV substrate peak characteristic of the chemical cleanness of the sample after preparation. One can note on the second spectrum that the intensity of pure silicon is weakly attenuated after silicide formation, while an Auger peak signature of Mg appears. The energy position of
this Mg\textsubscript{43.5eV} peak is slightly different from the signature of pure magnesium Mg\textsubscript{45eV}. It has been stated as corresponding to Mg atoms in a Mg\textsubscript{2}Si binding environment\cite{18} and reveals the formation of a Mg\textsubscript{2}Si silicide thin film with high chemical purity.

**Figure 1.** (B), (C), (D) display AES spectra showing the formation process of silicide films with various thicknesses, before (black curves) and after (red curves) 200°C annealing of 1 Mg deposited monolayer (thickness of 0.3 nm), 4 Mg MLs (about 1 nm thick) and 8 Mg MLs (about 2 nm thick) respectively.

Note that an accurate calibration of the Mg deposition was stated by AES and STM in a previous work, together with a Frank van der Merwe growth mode for Mg on Si(100) at RT\cite{1}.

One can firstly observe for each AES plot that the silicon Auger peak exhibits stronger intensity after silicide film formation, while it is slightly, partially or almost completely attenuated as a result of Mg deposition at RT in Figs. (B), (C) and (D) respectively. This behavior confirms that a 200°C annealing induces an intermixing between Mg and Si species via reactive diffusion, i.e. magnesium silicide formation.

As previously shown in the early stages of deposition at RT, magnesium reacts to form a self-limited ultra-thin layer of Mg\textsubscript{2}Si on Si(100) up to 0.25 Mg deposited ML\cite{1}. Upon further deposition, this silicide behaves as a reaction barrier preventing the reactants from coming into contact, so that Mg metal starts growing on top of the interfacial silicide\cite{19}. Here, we report that 200°C thermal treatment allows Mg atoms to overcome this interfacial barrier to form thicker silicide films. The silicidation is clearly shown in Figure 1 (B), (C) and (D) with an observable Auger peak-shift for the Mg signal, from 45 eV (metal Mg) after deposition up to 43.5 eV (silicide Mg) after annealing.

The Si/Mg Auger peak-to-peak intensity ratio is measured to be 2 after annealing for the thinnest Mg deposition in Fig.1(B). This ratio decreases to 1.7 for thicker Mg quantities (Fig.1(C)) and remains at a constant value in Fig.1(C) and (D). This decrease of the Si/Mg ratio strongly indicates a substrate contribution in the signal intensity observed for silicon in Fig.1(B). Also, it suggests that the Mg\textsubscript{2}Si formed by annealing 1 Mg ML has not reached a complete coverage of the Si surface, or even that this silicide remains thin enough to not screen the signal contribution of the underlying substrate in AES.

Moreover, the Si/Mg Auger peak-to-peak ratio doesn’t evolve from (C) to (D), independently with the increasing of the deposited quantity between 4 Mg MLs and 8 Mg MLs. Assuming no more contribution of the underlying silicon for such coverages, this may reveal that the substrate is completely covered after at least 4 MLs of magnesium deposition (i.e. 1 Mg nm) and annealing. The thin Mg\textsubscript{2}Si film formed at this stage seems to be thick enough for totally screening the substrate contribution in the Si signal, beyond the limit of AES detection depth of around 3 nm.

**Figure 2** shows the dynamic evolution of the AES peak-to-peak signals that were monitored in-situ for Mg and Si species during the annealing process of 8 Mg MLs (~2 nm) deposited on
Si(100). A temperature ramp ranging between RT and 500°C was used to determine the three different processes: formation, stability and desorption of the thin silicide film. These AES curves clearly evidence three successive processes marked out by dashed lines. The first stage corresponds to the solid-phase reaction between the deposited Mg and the Si surface atoms. This thermally enhanced reaction is completed at 150°C, when the Mg₂Si film is totally formed by reactive diffusion between the Mg and Si species. The dynamic observation of such fast silicidation process becomes possible through a slow annealing ramp of about 10°C/min. Note that an Auger peak transition occurs for Mg in this region under Mg₂Si binding environment, which is not mentioned in Fig.2. The stage II depicts the stability window of this silicide film during further annealing at higher temperature. Fig.2 clearly demonstrates a higher thermal stability of the Mg₂Si silicide thin film formed by thermally enhanced solid-phase reaction, compared to other studies on ultra-thin films that proposed a Mg₂Si decomposition starting at 200°C with Mg desorption[20]. As suggested in stage III however, Mg₂Si decomposition finally starts when annealing temperature becomes higher than 350°C. A fast desorption process of magnesium species takes place at this stage, with no more AES Mg signal after 500°C. We underline that the silicide film formed by thermally enhanced solid-phase reaction of 8 Mg MLs exhibits in our case the same thermal stability window as thicker Mg₂Si films (80 and 600 nm thick) grown by thermal codeposition on a Si(111) substrate. Besides different synthesis approaches, similar thermal decomposition frontiers observed at different thicknesses may address a potential influence of the substrate orientation on the thermal stability, as previously discussed by Vantomme et al.[9].

Whatever the silicide film thicknesses investigated in this work (i.e. after silicidation of 1, 4 and 8 Mg MLs) and despite LEED analysis attempts made in the entire range of thermal stability, no long-range crystalline order could be probed for the Mg₂Si films between 200°C and 400°C. This is in agreement with the formation of highly disordered magnesium silicide features that was reported by Kubo et al., after 400°C annealing of an ultra-thin Mg film deposited on Si(100) slightly beyond saturation[11]. Also, the formation of polycrystalline thin Mg₂Si has previously been reported on both Si(100) and Si(111) by thermal codeposition[21] and reactive diffusion[8] at 200°C. Considering these results, our investigation may also indicate a small polycrystalline structure for the formed silicide thin films, i.e. nano-size crystalline domains of Mg2Si islands too small to observe with LEED.

**Figure 3.** (A) displays a wide (600 x 600nm²) empty state STM image recorded after silicide formation, obtained using a 200°C annealing of 1 Mg ML deposited on Si(100). The related height profile shown in the inset corresponds to the blue line drawn into the image. Here, Mg₂Si islands can be observed with a homogeneous height of approximately 3 nm and an average lateral size ranging between 20 and 50 nm. Fig.3(A) exhibits a discontinuous distribution, with several areas being uncovered between the silicide crystallites.". This is consistent with an increased Si/Mg Auger peak-to-peak ratio measured in Fig.1(B) for the
thinner deposited layer, thus indicating an increased contribution corresponding to the bare parts of the underlying silicon in the AES spectra. Thus, we assume that the thermally enhanced reaction of 1 Mg ML results in the appearance of Mg$_2$Si nanometric crystallites leaving the silicon surface partially uncovered.

Figure 3. (B) shows another wide (600 x 600nm$^2$) empty state STM image recorded after the formation of a thin silicide film obtained using a 200°C annealing of 4 Mg MLs (thickness about 1 nm) deposited on the Si surface. The silicidation of this thicker Mg layer results in the formation of a continuous Mg$_2$Si film with a complete coverage of the underlying substrate. This thin silicide film exhibits also a peculiar surface topography characteristic of a volcano shape that was similarly reported under SEM observation for thicker Mg$_2$Si films grown by reactive diffusion[22]. On the corresponding height profile, an average corrugation of about 9 nm can be measured from the deep valleys up to the topmost regions observed at the silicide surface. Note that Mg$_2$Si growth has previously been observed in a columnar fashion after 200-300°C solid-phase annealing of thicker Mg films on silicon (tens of nanometers range)[23]. This tendency could give insights regarding the existence of protrusions in the Mg$_2$Si layer. Our present report of a continuous thin silicide film, nevertheless, remains quite different from the Mg$_2$Si nanometric crystallites that were observed elsewhere by solid-phase reaction of 1 Mg nm on Si(111) on hot silicon[10]. Whereas similar nanometric islands are formed after thermally enhanced reaction of 1 Mg ML (i.e. 0.3 nm thick) in our case, it appears that thicker Mg deposition allows transiting through the continuous growth of a thin Mg$_2$Si film on Si(100) at 4 Mg MLs.

During the early attempts that were made for growing thin silicide films in this study, partial oxidation of some Mg$_2$Si surfaces could be observed, at room temperature and under the influence of oxygen residual contamination into the chamber. Similar oxidation mechanisms have previously been reported for thicker magnesium silicide films (tens to hundreds of nanometers range) as a consequence of Mg$_2$Si dissociation. Note that several experimental conditions were used in these cases, regarding the origin of the oxygen environment (presence or not of an oxygen-contaminated atmosphere) and the thermal activation brought to the system, namely at 300°C [8], over 400°C [24] and 450°C [13]. All these reports, however, were based on a static observation of the products of the oxidation reaction. To our knowledge, no dynamic investigation of the decomposition mechanism was ever proposed. In the following, we thus address the kinetic influence of thermal oxidation performed at very low oxygen pressure on a thin magnesium silicide film. More precisely, in-situ AES monitoring performed at both constant annealing temperature (T=200°C) and constant low pressure of molecular oxygen ($P_{O2}$= 5.10$^{-9}$ T) allows the dynamic observation of the Mg$_2$Si film decomposition induced by the thermal oxidation process.
Figure 4. (A) depicts AES spectra that give the surface chemical environment observed for the thin silicide film after the thermally enhanced silicidation reaction of 4 Mg MLs (i.e. 1 Mg nm) deposition and 200°C annealing (red curve) and as a result of 30 minutes of oxygen exposure (P\textsubscript{O2}= 5.10^{-9} T) while keeping the sample at the constant temperature of 200 °C (black curve). As suggested with the appearance of an O\textsubscript{511}eV Auger peak of high intensity on the black spectrum, the thin silicide film is drastically affected in the presence of an oxidized environment. Due to strong reactivity between the silicide Mg atoms and O adsorbed species, one can observe a noticeable peak-shift of 8.5 eV for the magnesium signal, from Mg\textsubscript{43.5}eV (under Mg\textsubscript{3}Si binding environment) up to Mg\textsubscript{35}eV under Mg oxide environment. Since no residual Mg quantity remains unoxidized at surface (complete vanishing of the Auger Mg silicide peak and no Auger pure Mg peak appearance), this thermally enhanced oxidation induces an entire decomposition of the silicide thin film to form a magnesium oxide film. Regarding the studies previously mentioned, we claim here the lowest-temperature of thermally enhanced decomposition process reported at 200°C. Note that various products of decomposition were also proposed in previous studies, such as a mixture between magnesium oxide and Mg dissociated species\cite{13}. In our case, the observation of a single oxidized Mg\textsubscript{35}eV peak (stated as characteristic of the pure MgO binding environment\cite{1}) may reveal the emergence at the surface of a single decomposition product within the limits of AES detection, i.e. the formation of a stoichiometric MgO film. It is interesting to note that no peak-shift is observed for the Si\textsubscript{92}eV signal that remains at its initial position before and after thermal oxidation. At very low oxygen pressure in this study, we therefore underline that this decomposition process prevents both the (100)-silicon surface and the dissociated Si species from oxidation, at least for annealing temperatures up to 200°C.

Figure 4. (B) displays Auger peak-to-peak intensities that were monitored in-situ for the Mg\textsubscript{43.5}eV (silicide Mg), Si\textsubscript{92}eV (silicon) and Mg\textsubscript{35}eV (oxidized Mg) signals, during a thermal oxidation that was performed in the same experimental conditions as Fig.4(A) (200°C, P\textsubscript{O2}= 5.10^{-9} T, 4 Mg MLs). The dashed line corresponds to the time at which the constant pressure of molecular oxygen was introduced into the chamber. Note that the AES signal of oxygen was deliberately not represented in this figure, for greater clarity.

In agreement with Fig.4. (A), one can first observe that the Mg\textsubscript{43.5}eV peak (corresponding to the silicide film) totally shifts towards the lower oxidized position Mg\textsubscript{35}eV after 9 minutes of oxidation process. For a better understanding, we mention that the O\textsubscript{511}eV signal (not represented) starts to increase as soon as a weak oxygen pressure is introduced into the chamber (i.e. after 5 min) and stops evolving after 18 minutes. The Si\textsubscript{92}eV peak is drastically attenuated as a result of magnesium oxide formation, while no peak-shift is observed during the process.

Regarding this dynamic evolution, we assume that the formation of a MgO film occurs through a mechanism of complete decomposition of the silicide thin film. Driven by the reactive adsorption of oxygen at the surface at the temperature of 200°C, decomposition may take place following the Mg\textsubscript{3}Si+O\textsubscript{2}→2MgO+Si equation. Under the Ellingham
approximation, we estimate a Gibbs energy of reaction equal to \(-1019.9\ kJ.mol^{-1}\) for this decomposition mechanism (see the standard values of formation enthalpy and entropy given elsewhere\([25,26]\)), meaning a strong probability of spontaneous occurrence at 200°C. Such mechanism of Mg\(_2\)Si dissociation to form MgO is therefore strongly supported by thermodynamics considerations. Regarding the corresponding reaction enthalpy of \(-1123.6\ kJ.mol^{-1}\), we underline a strongly exothermic reaction whose observable effects have previously been discussed at RT\([16]\). As mentioned above, several reports have been made on the decomposition of thicker silicide films by exposure to oxygen ambient. At high annealing temperature, it has been proposed that the formation of MgO as a reaction product relies on a balance between desorption of dissociated Mg species (from the silicide) and recondensation of these Mg species in their oxidized form at the surface, under oxygen-contaminated environment\([8]\). At lower temperature in the present study, we highlight this oxidation mechanism may take place within the range of thermal stability of the thin Mg\(_2\)Si silicide film, i.e. below the regime of Mg desorption. On this basis, we believe that MgO formation is mainly driven by a solid-state process where the Mg\(_2\)Si thin film is totally dissociated through the reactive adsorption of oxygen at the surface. Such solid-state mechanism may be due to stronger reactivity between oxygen and magnesium species.

4. Conclusions

In conclusion, we report the in-situ formation of Mg silicide thin films grown by thermally enhanced solid-phase reaction of few Mg monolayers deposited on Si (100) surface at room temperature (RT). Magnesium silicidation performed at 150°C allows formation of Mg\(_2\)Si silicide films with an entire coverage of the silicon substrate for deposited Mg thickness of 1 nm and above. Topographic STM images display flakes of Mg\(_2\)Si on silicon for one Mg monolayer and a quite different volcano shape for thicker silicide films. Silicide features are stable up to 350°C before a desorption process. We finally highlight the transition from a narrow-band-gap semiconductor Mg\(_2\)Si thin film (0.75 eV band gap) to a wide-band-gap insulating MgO film (close to 6 eV band gap for ultra-thin film) driven by an oxygen adsorption process. During the process, no oxidation of the silicon substrate is observed. This opens a road towards magnesium-based thin films with switchable electronic properties on silicon, by way of a controlled oxygen environment.

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Figure captions:

**FIG. 1.** (A): AES spectra recorded for the bare silicon surface and after formation of a Mg₂Si silicide layer by thermal silicidation reaction (annealing at 200°C of 2 nm thick Mg deposited on Si(100)). (B), (C), (D): AES spectra recorded after deposition of various Mg thicknesses on Si(100), respectively 0.3 nm, 1 nm and 2 nm (black curves) and corresponding spectra recorded after 200°C annealing (red curves).

**FIG. 2.**: Auger peak-to-peak signals of the Mg (black squares) and Si (red dots) species recorded as a function of annealing temperature, starting from 2 Mg nm deposited on Si (100) at RT. Note that a magnesium peak-shift occurs at the frontier of Mg₂Si formation shown in dash line on the image, from metallic Mg₄₅eV to silicide Mg₄₃.₅eV signature.

**FIG. 3.** (A): 600 x 600nm² empty state STM image (U=-0.8V, I=1nA) of 1 Mg monolayer (0.3nm) deposited on Si (100) and annealed at 200°C. (B): 600 x 600 nm² empty state STM image (U=-1.6V, I=0.5nA) of 1 Mg nanometer deposited on Si (100) and annealed at 200°C. The height profiles shown in the insets depict corrugation of the corresponding blue lines.

**FIG. 4.** (A): AES spectra recorded for the Mg₂Si silicide film formed by 1 Mg nm deposition on Si(100) and 200°C annealing (red spectrum) and as a result of 30 minutes of P₀₂= 5.10⁻⁹ Torr exposure at 200°C (black curve). (B): Auger peak-to-peak signals recorded for Si (red dots), Mg₄₃.₅eV in Mg₂Si (black squares) and oxidized Mg₃₅eV in MgO (blue triangles) species as a function of annealing time at constant temperature T=200°C under O₂ exposure. Note that oxygen was introduced at a constant pressure P₀₂= 5.10⁻⁹ Torr after 5 mins of annealing in (B), to ensure a homogeneous and stable temperature at the sample surface.