IN-SITU X-RAY DIFFRACTION STUDY OF THE U(MO)/SI SOLID STATE REACTION.

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ABSTRACT

The solid state reaction between U(Mo) and Si, leading to the formation of silicides, has been studied using in situ X-ray Diffraction. Samples were prepared by sputter depositing Si in thin layers on U(Mo) substrates and vice versa. Several samples were heated to temperatures up to 950 °C in a purified helium atmosphere. Even though the measurements were hampered by the undesired oxidation of uranium, the formation of various silicides could be observed. Kissinger analysis on ramp anneals with ramp rates of 0.2, 0.5, 1 and 3 °C/s have been performed to investigate the kinetics of the formed silicides. Using this method, the apparent activation energy for the different silicide formation reactions was deduced.

1 Introduction

Considering their technological importance, a lot of studies have been performed on the phase sequence and formation kinetics of silicides. In general, the kinetics of thermally activated processes can be described by means of the Arrhenius equation

$$k = Ae^{\frac{-Ea}{k_b T}}$$

$$\text{Eq. 1}$$

in which k is the growth rate coefficient, A is the pre-exponential factor (reaction coefficient) and *Ea* the apparent activation energy of the observed process. In order to experimentally determine

the *Ea* of the reaction, typically a series of isothermal measurements combined with Rutherford backscattering spectroscopy (RBS) and/or in-situ ramped resistance measurements can be used [1, 2, 3]. However, Kissinger analysis on the results obtained from in-situ X-ray diffraction (XRD) proves to be a more time efficient alternative to determine *Ea* [4, 5]. Instead of measuring the time needed at a fixed temperature to initiate the silicide formation, ramp anneals at different fixed heating rates are used to determine the apparent formation temperature at each ramp rate. The ramp rate determines the integrated thermal budget to which the sample has been exposed prior to reaching a certain temperature. The integrated thermal budget to reach a certain temperature will be much higher when using a relatively slow heating rate e.g. 0.2 °C /s instead of a faster heating rate e.g. 3 °C /s, because the sample will spend longer time at each temperature. As a result, the value of the apparent formation temperature will depend on the ramp rate.

By using the Kissinger equation [6] , which according to Colgan and d'Heurle [1] is applicable to ramp anneals,

$$\ln \frac{\frac{dT}{dt}}{T_f^2} = -\frac{E_a}{k_b T_f} + cst \qquad\qquad \textbf{Eq. 2}$$

the apparent *Ea* of the silicide formation process can be determined by plotting $\ln\frac{dT/dt}{T_f^2}$ as a function of $\frac{1}{k_b T_f}$. In this equation, T_f stands for the temperature of formation, which is taken as the temperature at which the rate of increase of the corresponding XRD peak intensity is maximal.

2   Experimental

Layers of U8wt%Mo having varying thicknesses (100nm, 500nm and 1μm) have been deposited by the Technische Universität München (TUM) on HF-cleaned Si substrates using physical vapor deposition (PVD) [7]. After the first high temperature experiments, a similar set of samples was prepared but additionally a 30 nm Si capping layer was deposited to prevent oxidation of the U(Mo) layer.

As part of the SELENIUM (Surface Engineered Low ENrIched Uranium-Molybdenum fuel) project, a sputter deposition setup was constructed in a collaboration between the University of Ghent and the SCK•CEN [8]. This coater has been used to deposit ~200nm thick Si layers on U(Mo) substrates. The U(Mo) substrates contain either 6, 8 or 10 wt % Mo and were kindly provided by the Atomic Energy of Canada Limited (AECL).

High temperature in-situ X-ray diffraction measurements are performed on a Brucker D8 Advance system equipped with a Våntec detector which allows for fast simultaneous recording of X-ray patterns over a wide 2θ angular range. The detector was used in snap shot mode, with a fixed 2θ range (25° - 45° 2θ). Phase transformation of the films was studied by ramp anneals from room temperature up to >850 °C at rates of 0.2, 0.5, 1 and 3 °C/s.

3 Results and discussion
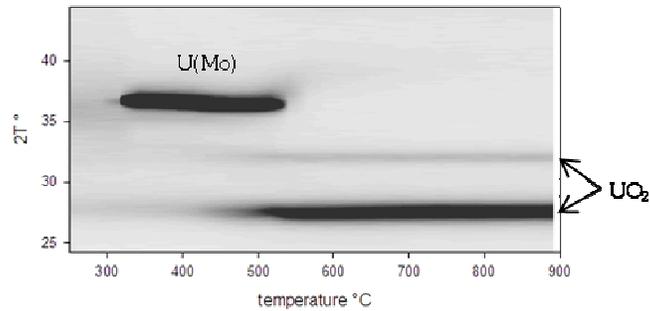
3.1 Si substrate/ U(Mo) layer

Figure 1 In-situ XRD results for ramp anneal of a Si substrate covered with 100 nm U(Mo) layer at a rate of 1 °C/s.

The scans of the Si substrate covered with 100 nm U(Mo), annealed up to 900 °C at a rate of 1 °C/s, shows the appearance of a peak around 37 °2T (Theta) at approximately 300 °C. This peak should be attributed to the crystallization of the sputtered (probably nanocrystalline) U(Mo) layer. Around 400-450 °C, the U(Mo) peak starts to disappear, indicating a reaction. At the same time two peaks emerge around 27 and 33 °2T. Detailed analyses show that these peaks can be attributed to the diffraction pattern of a UO_2 phase. Unfortunately there is no indication of silicides formation.

The U/UO_{2-x} equilibrium line is located at an extremely low oxygen potential (at 450 °C μ_{O_2} is

$\sim$ -960 kJ/mol), in that respect the high sensitivity of uranium for oxygen is understood. However, the annealing of the samples has been done either in vacuum (oxygen content <ppm) or under dry inert (He) atmosphere (oxygen content <ppb), so it is not clear where the oxygen originates from. A possible explanation could be that the adsorbed oxygen on the surface gets incorporated into the native UO_{2-x} lattice.

To prevent oxidation of the U(Mo) layer during the anneal, a second set of samples was prepared by TUM. This time the U(Mo) layers, again having varying thicknesses of 100nm, 500nm and 1μm, were finished off with a 30 nm thick Si layer. Even though that the Si/SiO_2 reaction has a higher oxygen potential then U/UO_2, Si passivates and therefore prevents oxides to reach the U(Mo) layer.
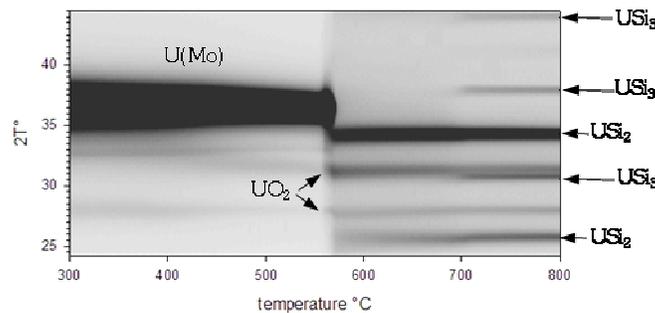

Figure 2 In-situ XRD results for ramp anneal of a Si substrate/ 500 nm U(Mo) layer/ 30 nm Si layer at a rate of 0.2 °C/s.

The in-situ XRD results (fig.2) of the Si substrate covered with a 500 nm U(Mo) layer/ 30 nm Si layer, show, again around 450 °C, the two UO_2 peaks at 27 and 33 °2T. These peaks become even more pronounced around 570 °C. However, at this temperature the broad U(Mo) peak at approximately 37 °2T disappears and several other peaks (next to the UO_2 peaks) become visible. The broad and intense peak around 34 °2T and the peak at 26 °2T indicate the growth of a crystalline USi_2 phase. With increasing annealing temperatures, more Si rich phases should be formed. This is observed at ~700 °C, where the peaks at 31, 38 and 44 °2T indicate the formation of a crystalline USi_3 compound.

In figure 3, the in-situ diffraction results at different ramp rates are shown. It is observed that the formation temperature of USi_2 (red markers) and USi_3 (green markers) increases with increasing ramp rate.
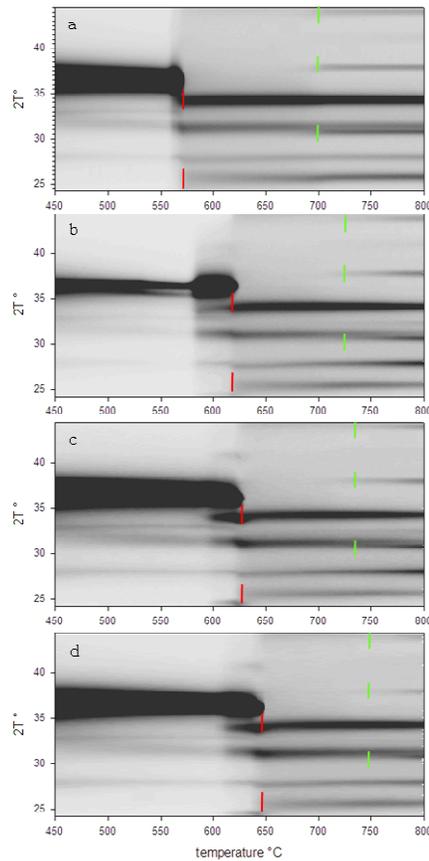

Figure 3 In-situ XRD results for ramp anneal of a Si substrate/ 500 nm U(Mo) layer/ 30 nm Si layer at a rate of a) 0.2 °C/s b) 0.5 °C/s c) 1°C/s and d) 3 °C/s. The red markers indicate the growth of a USi_2 phase while the green markers point out the formation of a USi_3 phase.

The T_f (temperature of formation) values for the different ramp rates were determined from the location of the maximum value of the first derivative of the integrated peak intensity versus the temperature (fig. 4).
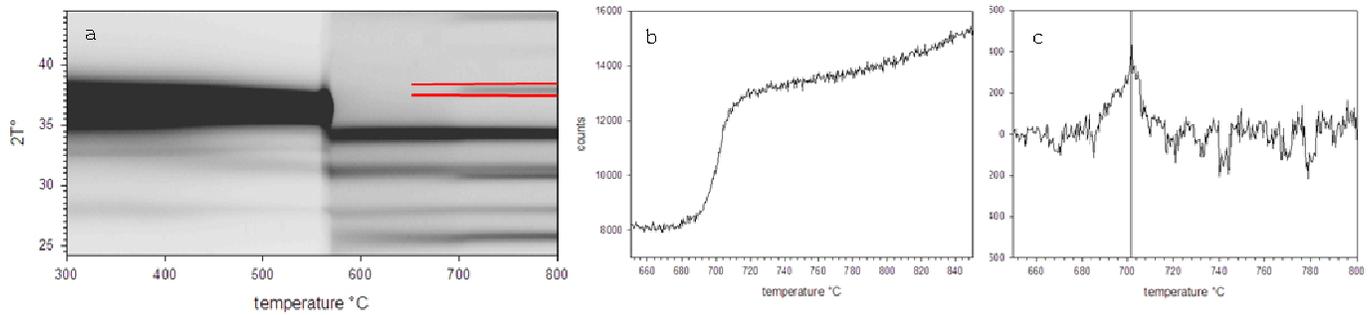
Figure 4 a) The (111) peak of USi₃ phase is defined (in-between red lines) and b) the integrated intensity of that peak is calculated. The maximum in the first derivative gives the formation temperature of the USi₃ phase at a ramp rate of 0.2 °C/s.

The measured temperature of formation T_f at the different ramp rates can be used to perform the Kissinger analysis (Eq.2) in order to determine the apparent activation analysis for the silicide formation. In figure 5, for each of the phases, —— is plotted as a function of —— . The apparent activation energy for USi₂ and USi₃ is determined from the slopes of the plotted lines and is respectively 3.5 ± 0.5 eV and 4.4 ± 0.6 eV.
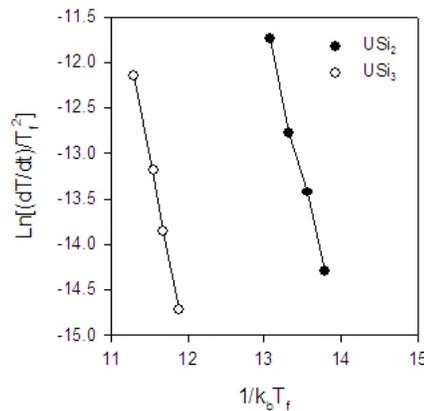

Figure 5 Kissinger plot of the silicide phases observed during the solid state reaction between 500 nm U(Mo) and Si using ramp anneals at 0.2, 0.5, 1 and 3 °C/s.

At first glance there seems to be no influence from the U(Mo) layer thickness but further analysis should confirm this.

3.2 U(Mo) substrate/Si layer

The HTXRD results (fig. 6) of the U8wt%Mo substrate covered with a 200 nm Si layer, show the presence of the UO_2 peaks even at lower temperature. This should be attributed to the native oxide layer that has formed on the surface of the U(Mo) substrate. Removing of this oxide layer can be achieved by dipping the surface in an acid. However, it was found that within seconds the oxide layer grew again and moreover the roughness of the polished surface increased substantially, giving rise to thicker oxide layer on average. It was decided to deposit a Si layer on the as-received (polished) U(Mo) substrates.
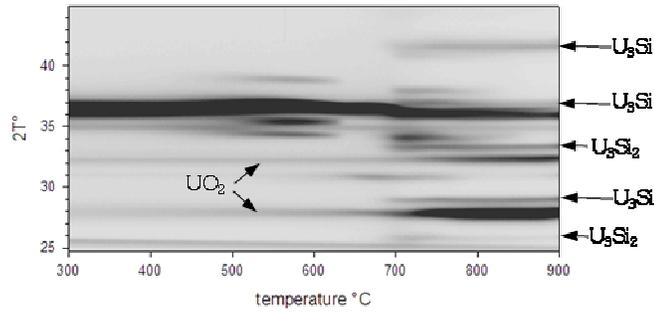
Figure 6 In-situ XRD results for ramp anneal of a U(Mo) substrate/ 200nm Si layer at a rate of 0.2 °C/s.

At a temperature of ~525 °C the decomposition of γ-U(Mo) (peak at 36.5 ° 2T) to α-U(Mo) is observed (peaks at 29, 35.5 and 38 °2T) but, as expected, at ~650 °C α-U(Mo) is transformed back to γ-U(Mo). At ~700 °C an almost simultaneous growth of multiple phases occurs. The peaks at 29, 36 and 42 º2T can be attributed to a U_3Si phase, while the peaks at 26 and 33 º2T point towards a U_3Si_2 phase.
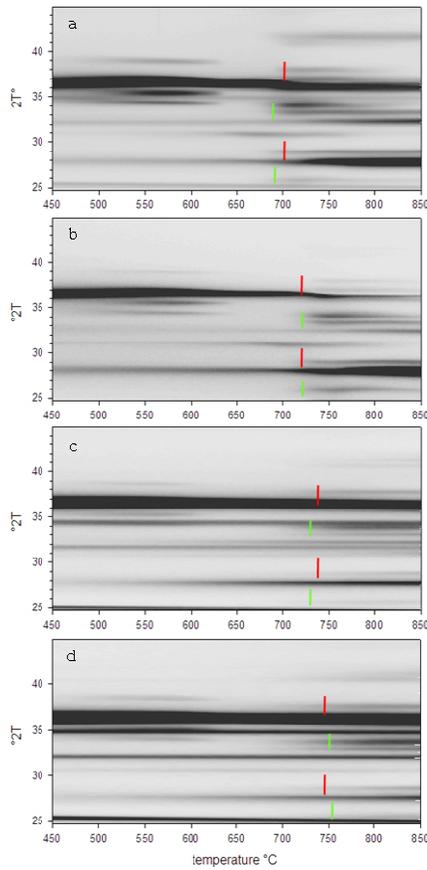

Figure 7 In-situ XRD results for ramp anneal of a U(Mo) substrate/ 200nm Si layer at a rate of a) 0.2 °C/s b) 0.5 °C/s c) 1°C/s and d) 3 °C/s. The red markers indicate the growth of a U_3Si phase while the green markers point out the formation of a U_3Si_2 phase.

The formation temperature of the U_3Si and U_3Si_2 phases at different ramp rates is determined from the in-situ diffraction results (fig.7), by means of the first derivative of the integrated peak intensity versus the temperature.
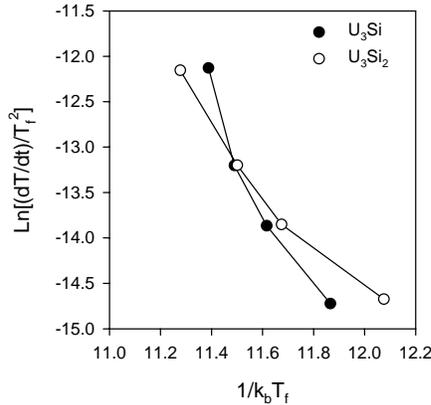

Figure 8 Kissinger plot of the silicide phases observed during the solid state reaction between 200 nm Si and U(Mo) using ramp anneals at 0.2, 0.5, 1 and 3 °C/s.

From the Kissinger plot (fig.8), the apparent activation energy *Ea* for U_3Si and U_3Si_2 can be determined and is respectively 5.1 ± 0.8 eV and 3.1 ± 0.3 eV.

The obtained values for the apparent activation analysis are comparable to the results found for other silicide formations [1, 2, 5]. However, the almost simultaneous growth of the U_3Si and U_3Si_2 phase is not fully understood. The presence of the oxide layer on the U(Mo) substrate on the sequence of the phase growth and the influence of the Mo content in the U(Mo) substrate, should be studied in more detail.

4   Conclusion

The solid state reaction between Si and U(Mo) was studied using in-situ X-ray diffraction. The growth of an USi_2 and USi_3 phase has been observed during the anneal of a Si substrate covered with a U(Mo) layer. U_3Si, U_3Si_2 and other still unidentified phases appeared during heating of a U(Mo) substrate covered with a Si layer. The apparent activation energy *Ea* for the formation of U_3Si_2, USi_2, USi_3 and U_3Si, was determined with the use of Kissinger plots and equals respectively 3.1 ± 0.3, 3.5 ± 0.5, 4.4 ± 0.6 and 5.1 ± 0.8 eV.

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