Thin Solid Films 542 (2013) 210–213

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Interactions of C in layered Mo–Si structures ☆

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ARTICLE INFO

Article history:
Received 19 April 2013
Received in revised form 30 May 2013
Accepted 30 June 2013
Available online 6 July 2013

Keywords:
Nanoscale interdiffusion
Thermal stability
Mo/Si multilayer mirror

ABSTRACT

Interdiffusion of a few nanometers thick C layer with Mo and Si under annealing at a temperature of 600 °C was studied using X-ray photoelectron spectroscopy sputter depth profiling. A strong diffusion asymmetry of C in a Mo–Si layered structure is observed. C does interdiffuse with Mo, however, even at 600 °C, no interdiffusion of Si and C was observed. Based on these results, the thermal stability of Mo/Si-based layer structures was improved by depositing a Si/C/Mo_2C/C/Si layer structure. This structure shows superior thermal stability at 600 °C compared to the Mo_2C/Si and Mo/Si layer structure.

1. Introduction

Mo/Si multilayer structures as Bragg reflectors for Extreme Ultra-Violet radiation (EUV) have been studied widely. However, two key issues in these multilayer structures still require further study: interlayer formation during deposition and interdiffusion of the materials under thermal load of for example 92 eV radiation for EUV lithography. Both effects reduce the optical contrast between the layers, and thereby reduce the peak reflectance. It has been observed that both the initial interlayer width and the interdiffusion rate are largest at the Mo-on-Si interface [1]. Additionally, the growth of the interlayers during annealing can not be described by the usually assumed parabolic growth (i.e. the squared interlayer width is proportional to time). There is a transition from anomalous to parabolic growth. During this transition, the diffusion rate reduces and the activation energy for interdiffusion at the Si-on-Mo interface increases from 1.7 to 2.5 eV, whereas at the Mo-on-Si interface the activation energy remains constant at 2.5 eV [2].

To reduce interdiffusion of Mo and Si it is common to put an additional barrier layer in between Mo and Si. This layer should have three properties: (1) chemically stable; (2) low interdiffusion rates with Mo and Si; (3) preferably a positive, otherwise a not too large negative effect on the reflection. The last requirement usually means that the additional layer should be very thin, usually a few tenths of a nanometer.

Reported compositions for this diffusion barrier layer are Si_3N_4, Mo_2C, and B_4C [3–5]. A thin B_4C layer significantly prevents interdiffusion up to 400 °C [6]. For higher temperatures, the multilayer structures started to degrade. For annealing temperatures around 500 °C, the B_4C layer decomposes and reacts with Mo and Si [7]. They speculate that a SiB_xC_y layer is formed, which is responsible for the thermal stability in Mo/Si multilayer structures containing B_4C barrier layers.

In this research we focus on the properties of a thin C layer in a Mo–Si layered structure, since: (1) for B and C there is a chemical driving force to intermix with Mo and Si (i.e. both have a negative enthalpy of formation with Mo and Si). However, the melt temperature for C is much higher than for B_4C, 3800 K vs 2445–3036 K. Therefore, a C layer might be more stable in this layer structure with Mo and Si; (2) like B_4C, a thin C layer slightly increases the reflectance of Mo/Si multilayer structures [8]. In both cases, this is likely due to the reduction of initial interdiffusion of Mo and Si. From optical point of view, this makes C, like B_4C, also a suitable candidate to be used in practice as a barrier layer between Mo and Si.

Furthermore, to passivate an entire layer in order to reduce interdiffusion, the Mo layer can be replaced by Mo_2C [9]. Although these multilayer structures were much more stable than the standard Mo/Si structures, the structure still degrades above 500 °C. Based on our gained knowledge on C interactions in a Mo–Si structure, described in this paper, we discuss a method to improve the Mo_2C/Si layer structure and to further reduce interdiffusion of Si into the Mo–carbide layer, especially during annealing.

2. Experimental details

Samples containing C, Mo and Si were deposited onto super polished Si (100) wafers using electron beam evaporation. For

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2013.06.082

electron beam evaporation, the arriving particles have a relatively low energy (0.1–0.2 eV). Therefore, intermixing at interfaces due to ballistical effects is minimized. To modify the density of the layers, after 1 nm of deposited material, a Kr ion beam was switched on (beam voltage 80 V, flux 7×10^{13} cm^{-2} s^{-2}, angle of incidence 45°) for the remainder of the layer. All samples were deposited at a base pressure lower than $2 \cdot 10^{-6}$ Pa. The film growth was monitored by quartz crystal microbalances.

All samples were analyzed using X-ray photoelectron spectroscopy (XPS) Thermo Scientific Theta Probe instrument, using monochromatic Al K_α radiation. To study interdiffusion of C, Mo and Si, XPS sputter depth profiling (0.5 keV Ar^+ at 45°) was used before and after annealing at 500 or 600 °C. Four types of trilayer structures have been studied:

- substrate/Mo(10 nm)/C(4 nm)/Mo(10 nm)
- substrate/Si(10 nm)/C(4 nm)/Si(10 nm)
- substrate/Mo(10 nm)/C(2 nm)/Si(5 nm)
- substrate/Si(10 nm)/C(2 nm)/Mo(5 nm).

Based on the results of the previous series of samples, an additional series of samples was deposited and analyzed in the same manner:

- substrate/Si(10 nm)/Mo_2C(5 nm)/Si(10 nm)
- substrate/Si(10 nm)/C(2 nm)/Mo_2C(5 nm)/C(2 nm)/Si(10 nm)

To ensure the correct stoichiometry of the carbide layer, the Mo_2C layers were deposited using magnetron sputtering.

3. Results and discussion

3.1. Diffusion of C in Mo and Si layered structures

To study the effect of a thin C layer with Mo and Si, we first investigate the interaction of C with only Mo or Si. For this purpose, XPS sputter depth profiles of as deposited and annealed (1 h) Si/C/Si and Mo/C/Mo structures were measured. The XPS sputter depth profiles are illustrated in Fig. 1(a) and (b). The depth scale (x-axis) is based on thicknesses determined by the quartz crystal microbalances and a constant sputter rate for every material. At 500 °C, Mo and C interdiffuse, whereas even at 600 °C we observe no interdiffusion of Si and C. Therefore, in the more complex structures where a C layer is in between Mo and Si, we can expect a strong diffusion asymmetry of the C.

In Fig. 2(a) and (b) the XPS sputter depth profiles of Si(wafer)/Si/C/Mo and Si(wafer)/Mo/C/Si layered structures are illustrated. For the as deposited structures it is clear that the carbon distribution for the Mo on C on Si is broader with a lower maximum than for the Si on C on Mo structure. This is usually interpreted as a more in depth localized carbon concentration, which suggests that the carbide interlayers are smaller for the second structure. This is in agreement with the usually observed asymmetry of interlayer widths in Mo/Si multilayer systems. In these structures, the Mo-on-Si interlayer is thicker than the Si-on-Mo interlayer [10].

The depth profile of the Si (wafer)/Si/C/Mo structure annealed at 600 °C for 3 h, shows that C has fully diffused into the Mo layer and on average has formed a homogeneous layer with Mo. The Mo/C ratio is approximately 2/1, suggesting that an amorphous or crystalline Mo_2C has formed. Nakanishi et al. have shown that indeed annealing at 600 °C for 1 h of a Mo/C (diamond) layer structure leads to a 3–4 nm thick amorphous layer with crystalline Mo_2C and

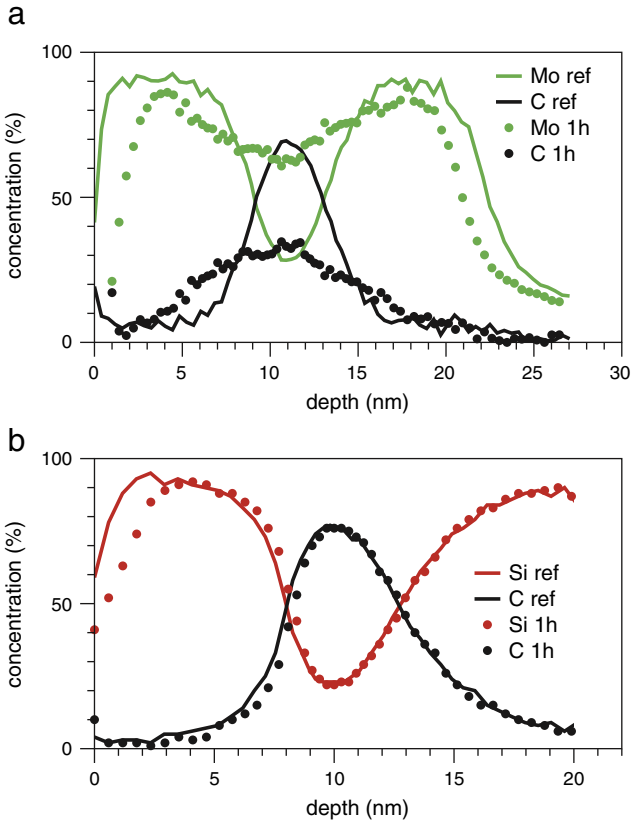

Fig. 1. XPS sputter depth profile of: (a) Mo/C/Mo before (solid line) and after (dotted line) annealing at 500 °C for 1 h; (b) Si/C/Si before (solid line) and after (dots) annealing at 600 °C for 1 h.

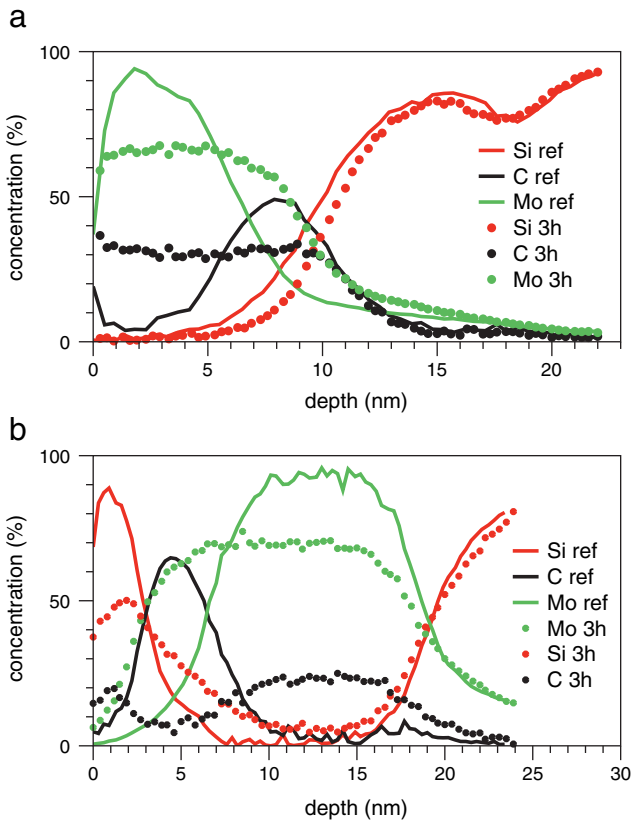

Fig. 2. XPS sputter depth profile of: (a) Si(wafer)/Si/C/Mo before (solid line) and after (dots) annealing at 600 °C for 3 h; (b) Si(wafer)/Mo/C/Si before (solid line) and after (dots) annealing at 600 °C for 3 h.