Interface Evolution in a W/Si Multilayer after Rapid Thermal Annealing Studied by X-ray Reflectivity and Diffuse Scattering

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Abstract

An interface study of the effect of rapid thermal annealing (RTA) in the temperature range 523–1273 K for 5–40 s on a nominally [(50 Å Si/10 Å W) × 9] amorphous multilayer (ML) deposited on an Si(100) wafer was performed by X-ray reflectivity and diffuse-scattering measurements at grazing incidence. The results of the X-ray reflectivity and diffuse-scattering measurements were evaluated by Fresnel optical computational code and within the distorted-wave Born approximation, respectively. Up to the 773 K/5 s annealing step, the r.m.s. interface roughness decreases by 30%, which brings about a reflectivity increase of 20% on the first Bragg maximum. There is a small overall increase of the r.m.s. interface roughness across the ML in the as-deposited state and the interface profiles are highly correlated. From the very beginning of RTA, the fractal interface behaviour is gradually lost and the lateral correlation length increases, this process being accompanied by a decrease of the interface conformality. This tendency continues during the 773 K/20 s annealing; however, the r.m.s. roughness evolution is reversed. During the 1023 K/5 s annealing, the interfaces are no longer 'seen' by the X-rays and, during the 1273 K/5 s annealing, a total collapse of the ML structure takes place.

1. Introduction

Refractory metal/Si multilayers have attracted much attention recently because of their potential applications in X–UV optics and very large scale integration (VLSI) technology. Thermal loading may degrade the optical properties of a multilayer (ML). Therefore, knowledge of thermal stability and interface evolution in these multilayers at elevated temperatures is of crucial importance. In this paper, we consider this topic with regard to W/Si multilayers.

2. Experimental

The samples were prepared by UHV electron-beam evaporation on Si(100) wafers in a Balzers 500

apparatus. The deposition started with Si and nine repetitions of the nominally (50 Å Si/10 Å W) bilayer were grown. The X-ray diffraction measurements showed that the internal structure of the layers is amorphous.

The X-ray reflectivity and diffuse-scattering measurements at grazing incidence were performed with a Stoe high-resolution diffractometer equipped with a double-crystal GaAs monochromator, working on the 400 reflection and using Cu K α_1 radiation (for details, see Brunel *et al.*, 1993).

The RTA was performed on different pieces of the same sample in a halogen-lamp vacuum furnace (pressure 10^{−3} Pa) in the temperature range 523–1273 K for 5–40 s. The heating rate was 50–100 K s^{−1}.

3. Theoretical background

A well established and predominantly used approach for the evaluation of X-ray reflectivity is based on the Fresnel optical theory (Underwood & Barbee, 1981). When measuring the reflectivity, the scattering vector is perpendicular to the interfaces so that no distinction between graded (interdiffused) and truly rough interfaces can be made. More information may be obtained in a geometry with a nonzero lateral (along an interface) component of the scattering vector. In this geometry, the scattering is due solely to the 'true' interface roughness (diffuse scattering).

The distorted-wave Born approximation (DWBA) proved to be a proper approach to simulate the interface (surface) diffuse scattering not far above the critical angle for the total external reflection (TER), θ_c , where the Fresnel states still represent a proper description of the system (Sinha, Sirota, Garoff & Stanley, 1988; Holý, Kuběna, Ohlídal, Lischka & Plotz, 1993). The essence of the DWBA is the division of the scattering potential into two parts, namely the undisturbed system (ideal interface) and a small disturbance (roughness). Consequently, perturbation theory is used to solve the wave equation under the condition $q_z\sigma \leq 1$, where q_z and σ are the z component of the scattering vector oriented perpendicularly to the interfaces and the root-mean-square (r.m.s.) interface roughness, respectively. The resulting differen-

tial cross section is composed of the coherent (specular) and incoherent (diffuse) terms. The former represents the transitions between two ideal (*i.e.* Fresnel) states averaged over the statistical ensemble of all the defect configurations of the surface and provides the plane part of the emitted field, *i.e.* reflectivity. It was shown within the second-order DWBA that the reflectivity depends, though very weakly, on the lateral interface parameters too (de Boer, 1994). The second term of the differential cross section is connected with the transitions between two ideal states on the disturbance potential and produces scattering into the whole solid angle (diffuse scattering).

A proper interface (surface) morphology description is necessary for the disturbance potential. For self-affine isotropic solid thin-film surfaces and interfaces with cut-off, the height–height self-correlation function

$$C(r) = \sigma^2 \exp[-(r/\xi)^{2h}] \quad (1)$$

proved to be a proper choice (Sinha, Sirota, Garoff & Stanley, 1988). Here, r , ξ and h are the lateral distance (along an interface), the lateral correlation length and the fractal parameter, respectively, the latter being related to the fractal dimension D of an interface by $D = 3 - h$.

In the case of an ML, the distribution of the diffuse intensity in reciprocal space is crucially dependent on the degree of the conformality of the interface profiles (Holý & Baumbach, 1994). Generally, a higher degree of conformality results in increased intensity concentration around the ML Bragg maxima (BM) of different orders.

Fig. 1. The trajectories of the different scans to trace the distribution of the scattered intensity at grazing incidence in the reciprocal space, calculated for $\text{Cu K}\alpha_1$ radiation and the decrement of the ML mean refractive index $\delta = 28 \times 10^{-6}$: (a) specular (reflectivity) scan; (b) offset scan; (c) sample scan (rocking curve); (d) detector scan. The stripes of the resonant diffuse scattering are shown schematically by broken lines around the full circles that represent the Bragg points of the ML, with the period $d = 45 \text{ \AA}$.

There are two groups of models describing the interface conformality. The models of noncumulative roughness (*e.g.* Ming *et al.*, 1993) express the cross-correlation function between two interfaces as a simple (usually exponential) attenuation of the geometrical average of their self-correlation functions with no regard to the microscopic mechanism of the ML growth. The models of cumulative roughness (*e.g.* Spiller, Stearns & Krumrey, 1993) suppose a part of the interface roughness to be replicated from the underlying interface according to a replication factor and another part coming from the deposition process itself (intrinsic roughness):

$$z_j = z_{j+1} * a_j + z^{\text{int}}. \quad (2)$$

The indexing starts from the surface and z_j represents the deviation from a perfectly smooth reference plane at the (x, y) position along the interface. a_j and z^{int} are the replication factor and intrinsic deviation from the reference plane, respectively.

4. Results

The distribution of the diffuse intensity in reciprocal space may be traced by different scans, as shown schematically in Fig. 1. In addition to the specular scan (reflectivity), sample (with the detector fixed), detector (with the sample fixed) and offset scans may be measured, the offset scan like the reflectivity but with

Fig. 2. The reflectivities of (a) the as-deposited ML and (b) 523 K/10 s, (c) 773 K/5 s, (d) 773 K/20 s and (e) 1023 K/5 s annealings. Dots indicate measured points and full lines represent simulations. The curves (b), (c), (d) and (e) are shifted upwards by factors of 10^2 , 10^4 , 10^7 and 10^{10} , respectively.

an offset from the specular position. The components q_x and q_z of the scattering vector along and perpendicular to the interfaces, respectively, are given by

$$\begin{aligned} q_x &= k(\cos \theta_o - \cos \theta_i) \\ q_z &= k[(n^2 - \cos^2 \theta_i)^{1/2} + (n^2 - \cos^2 \theta_o)^{1/2}], \end{aligned} \quad (3)$$

where n , θ_i and θ_o are the mean refractive index, the angle of incidence and the angle of exit, respectively, and $k = 2\pi/\lambda$ is the wavenumber. As the detector slit was wide open in the direction perpendicular to the scattering plane during the measurements, the measured intensity was integrated along the y axis. The stripes of the resonant diffuse scattering (RDS) around the ML Bragg points due to the interface conformality are also shown schematically in Fig. 1. They are kinematic in nature as they arise from the interferences on the vertically correlated interfaces when the condition $q_z = m(2\pi/d)$ is fulfilled, m and d being an integer (ML Bragg order) and ML period, respectively.

The reflectivity evolution on RTA documented for some chosen samples is presented in Fig. 2. Both BM, due to the ML periodicity, and Kiessig maxima in between, due to the thickness of the whole ML stack, are visible up to the 773 K/20 s annealing. On the 1023 K/5 s

annealing, only the latter modulations persist with a slowly changing envelope. Therefore, the ML stack is considerably degraded during this annealing with still no considerable interdiffusion with the substrate. The total collapse of the ML stack was observed on the 1273 K/5 s annealing. The experimental curves were simulated within the Fresnel theory and the effect of the interface imperfection was included by the attenuation factor $\exp(-16\pi^2\sigma^2 \sin \theta_i \sin \theta_r / \lambda^2)$, where θ_r is the angle of refraction. This factor corresponds to the error-function interface profile, which is probably no longer the most proper description for the 773 K/20 s annealing.

The diffuse scattering at grazing incidence was measured by sample and detector scans, with the detector and sample fixed at different ML Bragg orders and in between, respectively, which span a much wider interval of the interface roughness frequencies than an offset scan does. For illustration, in Fig. 3, the sample-scan results (rocking curves) for the samples of Fig. 2 are shown with the detector fixed at the second ML Bragg order, except for the sample annealed at 773 K/20 s where the second BM was suppressed. The detector scans taken at the second ML Bragg order of the as-deposited sample and on the 773 K/5 s annealing are shown in Fig. 4. The diffuse-scattering curves for one sample were simulated within the DWBA to a self-consistent result. The coherent and incoherent parts were calculated separately and put together. The starting value of the r.m.s. interface roughness was taken from the reflectivity simulations and proved to be slightly overestimated in comparison with the 'true' interface roughness determined from the nonspecular scans, which means that interdiffusion had taken place during the deposition process. The instru-

Fig. 3. The sample scans taken at (a) the second ML Bragg order on the as-deposited ML, and on the (b) 523 K/10 s and (c) 773 K/5 s annealings. For the 773 K/20 s treated sample, the sample scan (d) taken on the first ML Bragg order is shown. $\Delta\omega$ is the offset from the specular position. Dots indicate measured points and full lines represent simulations. The curves (b), (c) and (d) are shifted upwards by factors of 5×10^2 , 10^5 and 5×10^7 , respectively.

Fig. 4. The detector scans taken at the second ML Bragg order on the (a) as-deposited ML and on the (b) 773 K/5 s annealing. Dots indicate measured points and full lines represent simulations. The curve (b) is shifted upwards by a factor of 10^2 .

Table 1. *The simulation parameters of the RTA-treated samples*

δ and β are the decrements of the refractive index $n = 1 - \delta - i\beta$. Δ is the variation of the layer thicknesses across the ML providing the best simulation. The parameters shown without error estimates were fixed. Note that, owing to the Si diffusion into the W layers at RTA, the latter are no longer primarily composed of pure W, as discussed in the text.

RTA	No RTA	523 K/10 s	773 K/5 s	773 K/20 s
d_{Si} (Å)	54.0	48.7	47.4	33.0
d_{W} (Å)	17.0	21.0	21.7	30.0
$d_{\text{Si}} + d_{\text{W}}$ (Å)	71.0	69.7	69.1	63.0
Δ (%)	3	3	3	5
$10^6 \delta_{\text{Si}}$	7.58	7.58	7.58	7.58
$10^6 \delta_{\text{W}}$	45.26	41 (2)	40 (2)	32 (1)
$10^6 \beta_{\text{Si}}$	0.18	0.18	0.18	0.18
$10^6 \beta_{\text{W}}$	3.71	3.45 (10)	3.40 (10)	0.80 (5)
σ_N (Å)	5.0 (8)	3.5 (5)	3.0 (5)	3.5 (5)
σ_i (Å)	0.100 (5)	0.100 (5)	0.100 (5)	0.20 (1)
ξ (Å)	50 (10)	500 (100)	550 (100)	2000 (300)
L	0	100 (10)	150 (15)	300 (30)
h	0.20 (5)	0.75 (25)	0.75 (25)	0.75 (25)

mental resolution, the experimentally determined background and the primary-beam intensity, as well as the finite sample size affecting the intensity at small glancing angles, were incorporated into the simulations. For the sake of simplicity, no distinction between the W/Si and Si/W interfaces was made and the same type of self-correlation function was supposed for all the interfaces. The results are gathered in Table 1.

5. Discussion

The most distinct feature in the reflectivity curves is the suppression of the second BM on the 773 K/20 s annealing. This result points to a mutual convergence of the individual layer thicknesses; this development from the very beginning of RTA is evident also from Table 1. It is interesting that the r.m.s. interface roughness maintains a smaller value than in the as-deposited state up to the 773 K/20 s annealing and that the decrements of the refractive index of the W layers δ and β gradually decrease during RTA up to this annealing. Therefore, an RTA-induced interface shift into the Si layers without 'smearing-out' the interfaces may be supposed, owing to the diffusion of the Si atoms into the W layers, which grow at the expense of the Si layers. Simultaneously, the W layers become more polluted with Si, which lowers their δ and β values. In fact, Si is known as the faster diffusing species in the W-Si couple. We have recently found and analyzed in detail by *in situ* reflectivity measurements such a thermally activated interface shift in another W/Si ML (Jergel, Bochníček, Majková, Senderák & Luby, 1996). This interface shift is also responsible for a considerable reduction of the ML period $d = d_{\text{W}} + d_{\text{Si}}$, together with

the annealing-out of the excess free volume inherent to the amorphous structure.

The interface conformality in the as-deposited sample is directly recognizable from the detector scan (Fig. 4), from which the last maximum comes from the intersection of the scan trajectory with the RDS stripe around the third BM. The first maximum at $\theta_o = \theta_c$ is due to the surface resonant scattering caused by the surface roughness (Yoneda effect). The model of the vertical interface conformality presented by Holý & Baumbach (1994) was successfully used to simulate the results from the as-deposited sample. According to this model, the cross-correlation function between two interfaces is given by

$$K_{jk}(r) = K_N(r) + [N - \max(j, k)]D(r), \quad (4)$$

where N refers to the substrate and $D(r)$ is the lateral correlation function of the layer thicknesses with the same form as (1) but with σ replaced by ζ , which is the r.m.s. deviation of the probability distribution of layer thicknesses. In this model, the correlation lengths and fractal dimensions of the interfaces are the same, while the r.m.s. interface roughness increases towards the free surface according to

$$\sigma_j = [\sigma_N^2 + (N - j)\zeta^2]^{1/2} \quad (5)$$

owing to the intrinsic contribution of the deposition process itself. Thus, in the result, the interfaces are fully correlated though not identical.

A different situation occurs for the RTA-treated samples where somewhat weaker RDS is seen in the detector scans (Fig. 4). The model of cumulative roughness with adjustable strength of the interface conformality proposed by Spiller, Stearns & Krumrey (1993) had to be used to obtain satisfactory simulations, from which we derived the following relations:

$$\sigma_j^2 = (\sigma_N^2 \xi_N^2)/[\xi_N^2 + 4L^2(N - j)] + \sigma_i^2 \xi_i^2 \sum_{k=j+1}^N 1/[\xi_i^2 + 4L^2(N - k)] \quad (6)$$

$$\xi_j = [\sigma_N^2 \xi_N^2 + \sigma_i^2 \xi_i^2(N - j)] \times \left\{ (\sigma_N^2 \xi_N^2)/[\xi_N^2 + 4L^2(N - j)]^{1/2} + \sigma_i^2 \xi_i^2 \sum_{k=j+1}^N 1/[\xi_i^2 + 4L^2(N - k)]^{1/2} \right\}^{-1} \quad (7)$$

where σ_i and ξ_i are the intrinsic contributions and L represents the replication factor, e.g. for $h = 1$,

$$a_j = [1/(2\pi L^2)] \exp[-r^2/(2L^2)], \quad (8)$$

and controls the strength of the vertical interface conformality. Referring to the original notation of Spiller,

Stearns & Krumrey (1993), $L = (v_j t_j)^{1/2}$ and represents an effective value common to all the interfaces. To simplify the calculations, we also supposed constant values of σ_i and ξ_i for all the layers. We found that for $L = 0$, when the replication factor is a δ function and the convolution in (2) is replaced by a simple multiplication so that the conformality strength is at a maximum, the result for the as-deposited sample is the same as that stemming from the model of Holý & Baumbach (1994). It is obvious that (6) for $L = 0$ is identical to (5) for $\zeta = \sigma_i$ and (7) for $L = 0$ takes the form $\xi_j = \xi_N$.

For the RTA-treated samples, we had to decrease the strength of the vertical interface conformality by increasing L . We also had to modify the model by keeping the ξ_i values constant; otherwise, they would grow toward the free surface at a given L and cause the concentration of the intensity close to the specular beam to be too strong, this effect being more pronounced for larger L . The gradual smoothing of the interface profiles across an ML stack toward the free surface promoted by decreasing the interface conformality is a natural property of the model proposed by Spiller, Stearns & Krumrey (1993).

There are some interesting features to comment on in the rocking curves. In addition to the specular maximum broadened by the instrumental resolution and ML mosaicity, approximately S-shaped maxima are seen on the broader background of RDS when either $\theta_i = \theta_c$ or $\theta_o = \theta_c$. These so-called Bragg-like (BL) maxima have purely dynamic origin and have been explained by the concept of *Umweganregung* (Holý & Baumbach, 1994). The scattering process leading to a BL maximum is excited by another scattering process (diffuse scattering) when the standing-wave field in the sample is excited. The shape of a BL maximum depends on many factors, which have been discussed by Kaganer, Stepanov & Köhler (1995). To summarize, all the scattering effects observed in our diffuse-scattering measurements at grazing incidence were successfully simulated within the DWBA.

6. Conclusions

RTA treatment of the W/Si ML under study improves the interface quality up to the 773 K/5 s annealing. The r.m.s. roughness of the bottom interface decreases from 5 to 3 Å, which is accompanied by a reflectivity increase, e.g. of 20% on the first BM. The interface roughness increment across the ML introduced by the deposition

process is not affected up to this stage of RTA. The interface profiles are vertically highly correlated in the as-deposited state and exhibit fractal behaviour that shows a tendency to disappear from the very beginning of RTA. In fact, the simulation results changed negligibly when moving from $h = 0.5$ [exponential self-correlation function; see (1)] to $h = 1$ (Gaussian self-correlation function) so that the identity of the topological and fractal dimensions of the interfaces and the loss of the fractal behaviour cannot be concluded unambiguously. There is a gradual loss of the vertical interface conformality during RTA, connected with a large increase of the lateral correlation length of the interfaces, by more than one order of magnitude during the 773 K/5 s annealing.

During the 773 K/20 s annealing, an advanced interface shift into the Si layers within a still well preserved ML structure, connected with a further increase of the lateral correlation length, takes place, while the evolution of the r.m.s. interface roughness, which starts to increase, is reversed. On the 1023 K/5 s annealing, the interfaces are destroyed due to interdiffusion and intermixing and the ML is transformed to a thin film with a small concentration modulation remaining across it. This process is connected with the disappearance of the amorphous structure as, according to our previous studies (Brunel *et al.*, 1993), the formation of a tetragonal WSi_2 phase at the interfaces starts on RTA above 923 K.

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