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Residual Stresses in Mo/Si and Mo2C/Si Multilayers

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ABSTRACT

We report a study of the residual stresses and residual stress relaxation in Mo/Si and Mo_2C/Si EUV multilayers. The multilayers were fabricated by magnetron sputter deposition, and stress measured using the substrate curvature laser scanning technique. It was found that Mo_2C/Si multilayers exhibit higher compressive stress than Mo/Si of comparable period and layer thickness ratio. The multilayers sputtered at 0.5 mT Ar pressure have higher compressive stress than those sputtered at 2 mT Ar pressure. The data indicate that the residual stresses in the multilayers are primarily determined by the Si layers. Annealing of the multilayers at a heating rate of 5°C/minute as well as at a fixed temperature (isothermal) results in a reduction of the compressive stresses. Near zero stress is achieved after annealing at 300°C. The time dependence of the residual stress decrease during isothermal annealing was found to fit best to a bimolecular viscous flow model of defect annihilation in the amorphous Si layers. The relationships between the effects of annealing on the multilayer microstructure and the observed stress reduction are discussed.

KEYWORDS: Mo/Si, Mo_2C/Si, multilayers, residual stress, stress relaxation, annealing, viscous flow.

I. INTRODUCTION

Mo/Si and Mo_2C/Si multilayers have been used as normal incidence mirrors in the extreme ultra-violet (EUV) spectral region.[1-2] High performance multilayers are successfully deposited by the magnetron sputtering technique. Sputtering however usually produces films and multilayers with a high residual stress.[3-4] Residual stress usually depends on the sputtering conditions, e.g., gas pressure and deposition geometry; and film properties, e.g., thickness and microstructure, and interfaces in multilayer structures. In high spatial resolution EUV applications, stress-free or stable-stress multilayers are required as the presence of the residual stresses in the multilayers can distort the optic thus degrading performance. Understanding of the effects of deposition parameters on the residual stresses and the mechanisms for residual stress reduction either during deposition or by post-deposition treatments are therefore needed. In this paper, we report a study of the residual stresses in magnetron sputtered Mo/Si and Mo_2C/Si multilayers, and their dependence on the microstructure and annealing. In the remainder of the report, we will refer to the residual stress simply as stress for short unless otherwise noted.

Stress data in the literature so far focus mostly on single layer films or simple bilayer or trilayer structures. In a single layer film on a substrate, the stress depends primarily on the microstructure of the film resulting from film growth, and bonding between the film and the substrate. Similarly, the average stress in a bilayer or trilayer film includes the contribution from each layer, and also from the interactions at the interfaces between the layers. If the layers have opposite signs of stress, they counteract with each other which may result in a lower average stress than those in the individual layers. The interfacial contribution can also relieve or add to the average stress of the films. In EUV multilayer structures, a bilayer is repeated periodically to build up a stack of tens of bilayer pairs. In such a structure, the average stress in a bilayer of the multilayers is representative of that in the multilayered films, assuming that the microstructures and stresses in all the layers are identical, i.e., the microstructure and stresses in the layered stack do not vary with growth of the number of bilayer pairs.[5-6] Most reports thus present the multilayer stress data as a function of the multilayer period.

Preliminary studies of the residual stresses and microstructure in Mo/Si multilayers and their thermal behaviors have been reported.[5-12] Residual stresses in Mo_2C/Si multilayers however, to our knowledge, have not been studied. Previous reports showed that the residual stress in Mo/Si multilayers with a period ranging from 7 nm to 10 nm is compressive, and changes with multilayer periods.[7-9] The stress depends on γ, the ratio of the diffracting layer thickness to the multilayer period, and varies with the multilayer period or the microstructure in the layers.[8] The stress changes from compressive at low γ (thin Mo layer) to tensile at high γ (thicker Mo layer). The transition from compressive to tensile stress occurs at γ values between 0.5 and 0.6, depending on the deposition conditions.[5] Zero-stress Mo/Si multilayers hence can be obtained by controlling the relative thickness ratio in a multilayer period, though this condition typically results in reduction of the reflectivity.[6] Annealing of the multilayers results in permanent change in the stress resulting from reactions and phase transformation at the interfaces, densification due to crystallization and grain growth in the layers,[9,13-14] and possible stress relaxation due to viscous flow in the amorphous silicon layers.[7,9-10] From annealing experiments of Mo and Si films and Mo/Si multilayers, Kola et al. concluded that the stress relaxation in the Mo/Si multilayers results dominantly from that in the Si layers.[10]

In this paper, we report a study of the residual stresses in Mo/Si and Mo_2C/Si multilayers with deposition parameters. We will show that the stresses in these multilayers are primarily determined by the Si layers. We also report means of reducing the stresses in these multilayers by thermal annealing. We observed a stress relaxation in these multilayers at room temperature immediately after deposition, which prompts the isothermal stress annealing experiments at higher temperatures. At moderate temperatures, stress annealing studies show that the contribution of the Mo_2C and the Mo layers to the stress relaxation is negligible.[10,15-16] The stress relaxation in these multilayers is thus mostly dominated by the Si layers. We will show that the isothermal stress relaxation data fit best to a bimolecular viscous flow model of defect annihilation in amorphous silicon.

II. EXPERIMENTAL TECHNIQUES

The multilayers studied were deposited by dc-magnetron sputtering at Ar pressures of 0.5, 1, 1.5, and 2 mT. The substrates used were 4 inch prime (100) Si wafers. The base pressure of the chamber ranged from low-10^{-6} to high-10^{-7} Torr. The Si power was typically 400 W, the Mo 167 W, and Mo_2C 200 W. The first and the last layers of all multilayers were either Mo or Mo_2C, and all the multilayers were capped with a thin C layer to avoid oxidation. Thick Si and Mo_2C films were deposited layer by layer with the layer thickness equal to that of the 0.4-γ multilayers. The multilayer period and the total thickness of the multilayers were determined by low-angle x-ray diffraction and the number of bilayer pairs deposited. The thicknesses of the single films were measured using a Dektak profilometer.

The stress was determined using the laser-scanning wafer curvature measurement technique in a commercial Tencor (KLA) apparatus.[17] The thickness of each silicon wafer substrate was measured using an ellipsometer. The initial curvature of the Si substrates was determined and subtracted in the determination of the stress of the films. The stress in the films was calculated according to Stoney's formula.[18] *In-situ* thermal stress measurements were performed on a covered hot plate with a nitrogen flow over the surface of the samples for isolation. The heating and cooling rates were 5°C/minute and 10°C/minute, respectively. Isothermal curvature stress measurements were performed over a period of 12 hours at 100, 200, 300, 400, and 480°C. During the isothermal stress measurements, time, temperature, and substrate curvature were recorded.

III. VISCOUS FLOW MODELS OF DEFECT ANNIHILATION

Permanent stress change in the multilayers resulting from annealing results from structural changes and possibly relaxation of the amorphous Si layers to lower its free energy toward a more equilibrium state. This structural relaxation can be described macroscopically by viscous flow in amorphous materials whose mechanisms include unimolecular or bimolecular annihilation of the flow defects.[19] The macroscopic change can be observed by stress relaxation measurements according to the expression given by Witvrouw and Spaepen:[20-21]

$$\ln \sigma = \ln \sigma_o - \frac{E_f}{6(1-\nu_f)\cdot d\eta / dt} \cdot \ln\left(1 + \frac{d\eta / dt}{\eta_o} t\right),$$

where σ_o is the initial stress of the sample, and E_f and ν_f are the modulus and Poisson ratio, respectively, of the films. Previous studies of stress relaxation in glasses and covalently bonded amorphous structures, such as silica and amorphous silicon films, have demonstrated that the relaxation is best fitted with the bimolecular defect annihilation[19-23] that has an isothermal viscosity that increases linearly with time:

$$\eta(T,t) = \eta_o(T,0) + \frac{d\eta(T)}{dt} t.$$

In this study, we perform isothermal stress relaxation experiments in Mo/Si and Mo_2C/Si multilayers, and also found that the data fit best with the bimolecular relaxation equation.

The steps for analyzing the isothermal stress relaxation data to the viscous flow models are as followed. The change in the curvature ΔK was calculated by subtracting out the initial curvature in the substrate. Plots of $ln(\Delta K)$ as a function of time during the isothermal annealing were then plotted and analyzed using Igor Pro. The curves were smoothed using a binomial algorithm before being curve fitted with the exponential and log functions. The fit of the log functions provides the coefficients w[1] and w[2] from which $d\eta/dt$ and η_o can be calculated.[20-21] E_f and ν_f at different temperatures were calculated following Witvrouw and Spaepen.[20-21] η_o was treated as a fitting parameter to avoid biasing the fits with any transients which could have been present at the beginning of the anneals.

IV. RESULTS

RESIDUAL STRESSES AS A FUNCTION OF Ar PRESSURE

The residual stresses in Mo/Si and Mo_2C/Si multilayers, and in Mo, Mo_2C, and Si single films as a function of Ar sputtering pressure indicate that the stresses in the multilayers are primarily determined by the Si layers. Figure 1 shows the stresses in the Mo_2C and Si films and 6.9 nm period Mo_2C/Si multilayers deposited at 0.5, 1, and 2 mT Ar sputtering pressures. It can be observed that the films and multilayers sputtered at lower Ar sputtering pressure have higher compressive stresses than those at higher pressure. At the same sputtering pressures, the Mo_2C film has a higher compressive stress than the Si films, and both films have higher compressive stresses than the Mo_2C/Si multilayers. The multilayers with $\gamma = 0.2$ are more compressive than the multilayers with $\gamma = 0.4$, although their behaviors with pressure are very similar. This observation is consistent with previous results that show that the residual stress in Mo/Si multilayers is less compressive with increasing γ.[7-9] It is also observed that the behaviors of stress with pressure of the multilayers are more similar to those in the single Si films than the Mo_2C films, which suggests that the resultant stress of the multilayers is more dominated by the Si layers at these thicknesses.

Figure 2 plots the residual stresses in 6.9 nm period, 0.4–γ Mo/Si multilayers and in single Mo and Si films. The data of the Si films in this figure are the same as those plotted in Figure 1. Similar to the Mo_2C/Si results, the compressive stresses in the films and multilayers increase with decreasing Ar sputtering pressure. The Mo films however show a stronger dependence on sputtering pressure than the Si films and the Mo/Si multilayers. The stress behavior of the Mo/Si multilayers is also more similar to that of the Si films than of the Mo films. The stress in the 2 mT Mo/Si multilayer (-440 MPa) is about 13% lower than that in the 0.5 mT sample (-500 MPa). Figures 1 and 2 show that the Mo_2C/Si multilayers have higher compressive stresses than the Mo/Si multilayers of the same γ and deposited at the same Ar pressure.

The observation that the stresses in the multilayers are less compressive than the single films suggests that interactions at the interfaces in the multilayers relieve some of the compressive stresses in the layers. It is also possible however that the stresses in the layers in the multilayers are not the same as those in the thicker single films, in particular in the Mo and Mo_2C films whose microstructure changes significantly with thickness. At thicknesses in the range of a few nanometers, it has been reported that the stresses in sputtered Mo films are tensile, and become compressive as the film thickness increases.[7-8] Similarly, the stresses in the Mo and Mo_2C layers in the multilayers in this study may be less compressive or even tensile than those in thicker single films. They hence partially compensate for the compressive stress in the Si layers which results in lower compressive stressed multilayers.

STRESS RELAXATION BY THERMAL ANNEALING

Annealing of the multilayers was performed as a mean to reduce the compressive in the multilayers after deposition. After annealing at 500°C, both 6.9 nm period, 0.4-γ Mo/Si and Mo_2C/Si multilayers have a resultant tensile stress. Near zero stress is achieved after annealing to 300°C. The curvature of the samples and substrates was measured during the heating experiments, which also allows us to study the change in stress as a function of temperature. The stresses in the multilayers decrease elastically to about 100°C. The slope of this linear region corresponds to the difference between the average thermal expansion of the multilayer film and the Si substrate. Comparison of the slopes in the elastic regions during either heating or cooling at different temperatures hence provides a good indication of reactions and phase transformation in the multilayers. As temperature increases further, irreversible structural changes result in a more tensile stress resulting from densification in the layers, and reactions and phase transformation.[8-8] Figure 3 shows the stress annealing cycles of the Mo/Si multilayer with temperature to 150, 300, and 500°C. At temperatures below 250°C, the stress behaviors with temperature of the two multilayers are similar. As temperature increases, the stress in the Mo_2C/Si multilayer increases monotonically to almost 400 MPa at 500°C. Upon cooling, it increases further to more than 700 MPa at room temperature. The stress in the Mo/Si sample on the other hand increases more gradually after 250°C. A sharp dip is observed at about 460°C indicative of crystallization of a silicide phase at the interfaces that has been observed by TEM in previous studies.[8,14] Upon cooling from 500°C, the resultant stress of the Mo/Si multilayer is 1,080 MPa at room temperature.

The slopes of the cooling cycles at higher temperatures in the Mo_2C/Si multilayer are almost identical to that of the heating cycle from room temperature, which suggests that there are minimal changes in the microstructure or phases resulting from annealing. There is thus no indication of crystallization or phase transformation during annealing in Mo_2C/Si multilayers, consistent with cross-sectional TEM observation.[2] The Mo/Si multilayer on the other hand shows continuous change in the slope after annealing at 150, 300, and 500°C, which indicates different microstructures or phases in the multilayers after the anneals.

To study the contribution of the layers to the stress relaxation in the multilayers during annealing, we compare the stress dependence on temperature of the single films and the multilayers. Figure 4 plots the stress annealing results with temperature of single Mo_2C and Si films and a 0.4-γ Mo_2C/Si multilayers. In general, the stresses in all the samples become less compressive after annealing. The stress behavior with temperature of the multilayer sample is similar to that of the Si film, which suggests that the stress relaxation in this multilayer during annealing results mostly from relaxation in the Si layers. Kola et al. have performed

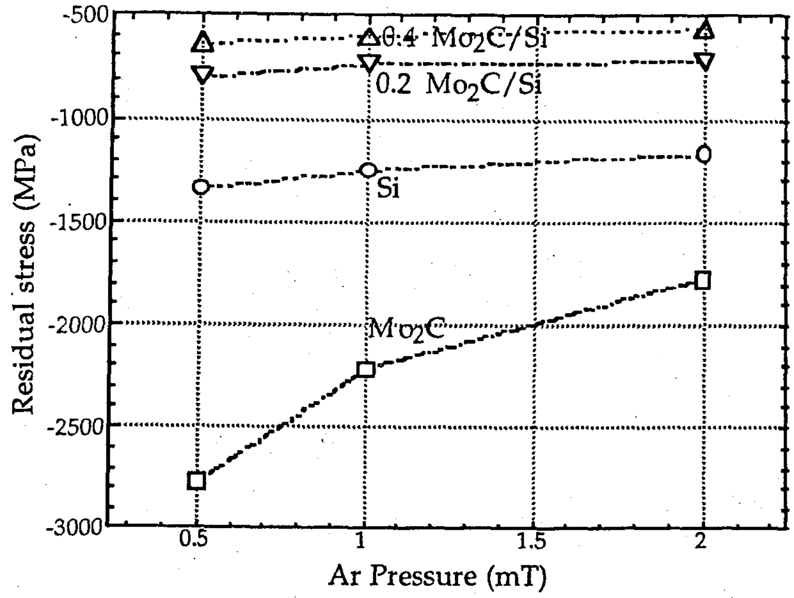

Figure 1. Residual stresses in Mo_2C/Si multilayers as a function of Ar sputtering pressure. The compressive stresses in the films sputtered at lower pressure are higher than those sputtered at higher pressure. The stresses in the multilayers is less compressive than those in the single Si and Mo_2C films and their trends with pressure follow that of the Si film. The lines are to guide the eyes.

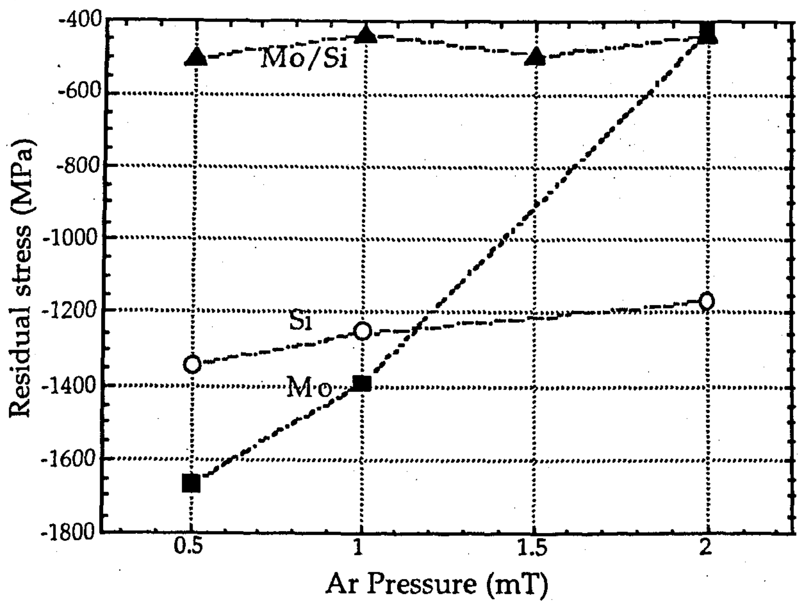

Figure 2. Residual stresses in Mo/Si multilayers as a function of Ar sputtering pressure. The stress in the Mo films show a strong dependence on Ar sputtering pressure.

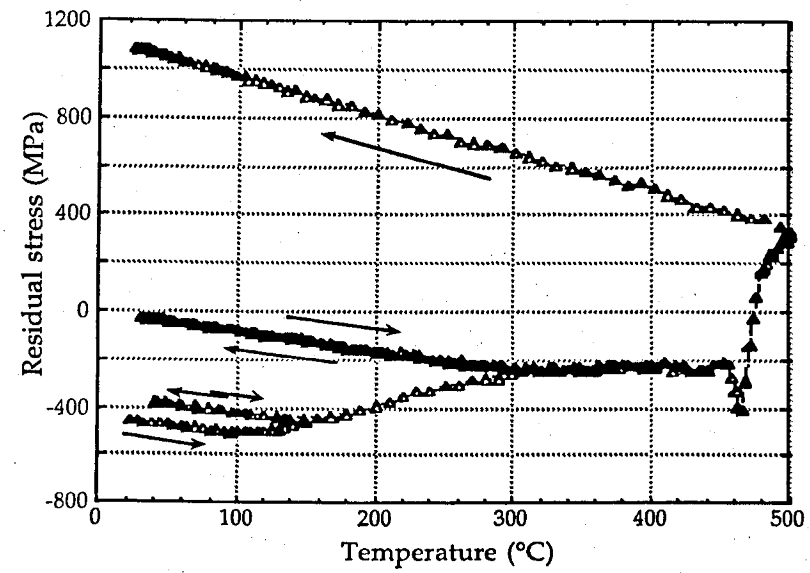

Figure 3. Cyclic stress anneals of a 6.9 nm-period 0.4-γ Mo/Si multilayer result in permanent change in stress. The stress is almost zero after annealing at 300°C. The dip near 460°C results from phase transformation/crystallization at the interfaces. The different slopes in the cooling curves at different temperatures indicate different thermal expansion coefficients resulting from different microstructures/phases.

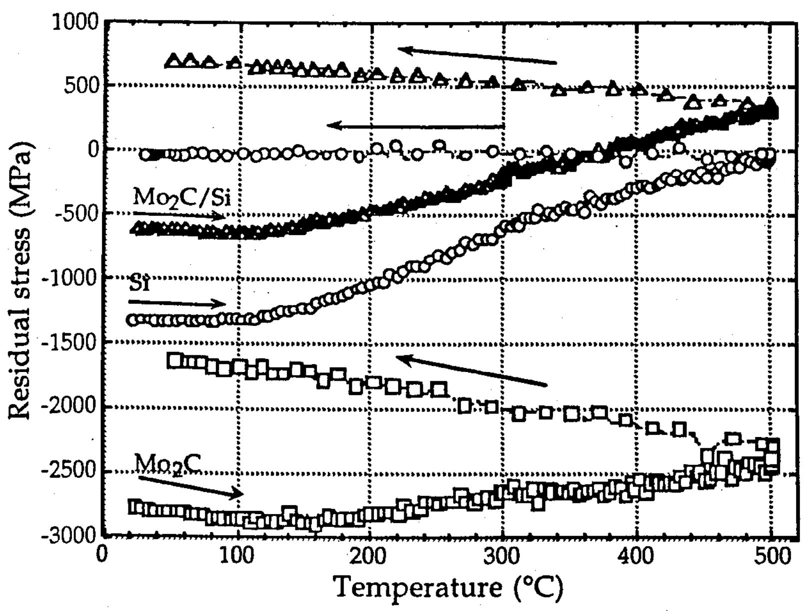

Figure 4. Stress behaviors of Mo_2C and Si films, and Mo_2C/Si multilayers as a function of temperature. All the films become more tensile upon annealing, and the multilayer shows similar thermal behavior as that of the Si film.

similar experiments on Mo and Si films and Mo/Si multilayers and also concluded that the stress relaxation in the Mo/Si multilayers results dominantly from that in the Si layers.[9]

Isothermal Stress Relaxation Experiments

We observe a reduction of compressive stress with time in all Mo/Si and Mo_2C/Si multilayers after deposition at room temperature. The stress changes dramatically over the first 15 days, and then more gradually toward an asymptotic value. Overall, we observed approximately 5% reduction in the compressive stress in Mo_2C/Si multilayers, and 10% reduction in Mo/Si multilayers after about 30 days. This observation has also been previously seen in 10 nm period Mo/Si multilayers.[24] We have also monitored the stress change in Mo_2C and Si single films and found that the change in Si films with time is similar to that observed in the multilayers, while the Mo_2C and Mo films do not show any observable changes. This observation of stress relaxation in the Si films and the multilayers at room temperature prompts the isothermal stress annealing experiments at higher temperatures whose preliminary results are followed. A full report on the isothermal stress relaxation experiments of Mo, Mo_2C, and Si films, and multilayers will be submitted in the future.

The *in-situ* thermal stress measurements of 6.9 nm period, 0.4-γ Mo/Si and Mo_2C/Si multilayers show similar stress behaviors at 300°C and lower temperatures. At these moderate temperatures, the isothermal stress measurements of both Mo/Si and Mo_2C/Si multilayers fit well with the stress relaxation of the bimolecular model. As an example, the data of $ln(\Delta K)$ as a function of time at 200°C for the Mo/Si and Mo_2C/Si multilayers and their fits to the bimolecular model are presented in Figures 5 and 6, respectively. The values of η_o, and $d\eta/dt$ of these samples is similar to those in the Si films at the same temperature. At higher temperatures, the isothermal stress data of the Mo_2C/Si multilayer can also be fitted with the bimolecular model. The Mo/Si multilayer, however, shows indication of crystallization and/or phase transformation during the isothermal anneal at 400°C, similar to that in the cyclic anneal of the same sample. This sample thus can not be fitted simply with a viscous flow model alone. Diffusion and crystallization have to be included in the model to fit the experimental data.

In the fits, the values for the modulus $E_f/(1-\nu_f)$ of Si films were used, since it was assumed that the stress change in both Mo and Mo_2C films is very minimal in this range of low temperatures. Also, it was assumed that the isothermal stress relaxation in the multilayers results dominantly from defect annihilation from viscous flow in the Si layers. To get a more accurate analysis of the data, the average moduli of the multilayers have to be determined. The most common method to determine the moduli in thin films and multilayers is the nano-indentation technique. We are in the process of using this technique to determine the moduli and the results will be presented in a future report.

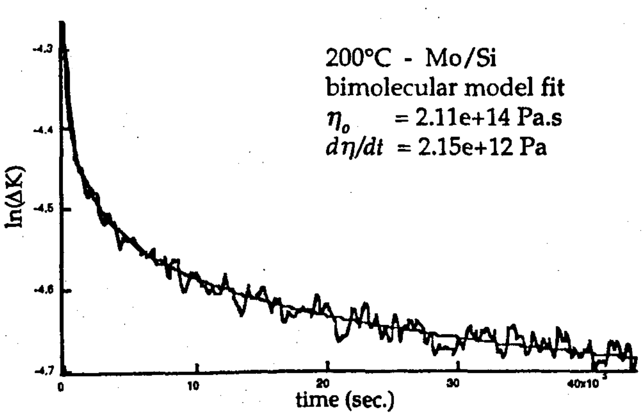

Figure 5. Bimolecular fit to the isothermal stress experiment of Mo/Si multilayer at 200°C.

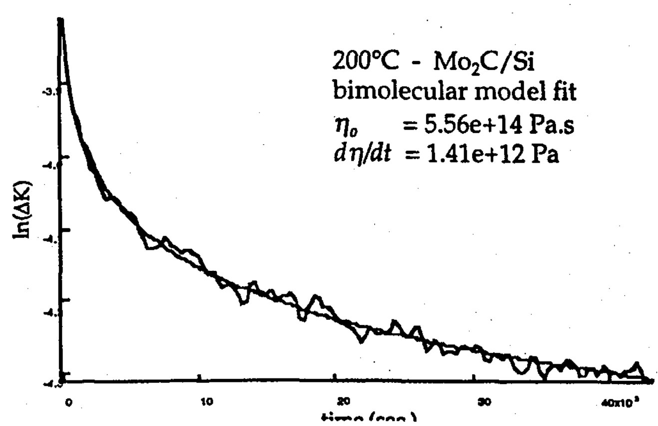

Figure 6. Bimolecular fit to the isothermal stress experiment of Mo_2C/Si multilayer at 200°C.

V. Conclusion

We have reported the results of a study of the residual stresses and their relaxation in Mo/Si and Mo_2C/Si multilayers. The average compressive stress in the multilayers is primarily determined by the Si layers. Mo_2C/Si multilayers exhibit higher compressive stress than Mo/Si multilayers of comparable period and layer ratio. Lower Ar sputtering pressure results in higher compressive stresses in similar multilayers. Isothermal stress relaxation experiments indicate that stress relaxation in the multilayers at 300°C and lower temperatures fits best to a bimolecular viscous flow model of defect annihilation in the amorphous Si layers. Annealing of the multilayers to 300°C reduces the compressive residual stress to near zero, and 500°C results in tensile stressed multilayers. Observation of stress changes as indications of crystallization of a silicide phase at around 400°C are seen in the Mo/Si multilayer, while no significant changes ~~is~~ are observed in the Mo_2C/Si multilayers. As a result, the layered structure in the Mo/Si multilayer degrades at temperatures beyond 300°C. The Mo_2C/Si multilayer, on the other hand, exhibits stable layered structure and compositional structure after annealing up to 500°C.

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