Stress relaxation in tungsten films by ion irradiation

E. Snoeks, K. S. Boutros, and J. Barone

Citation: Applied Physics Letters **71**, 267 (1997); doi: 10.1063/1.119515
View online: http://dx.doi.org/10.1063/1.119515
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/71/2?ver=pdfcov
Published by the AIP Publishing

Stress relaxation in tungsten films by ion irradiation

E. Snoeks,[a] K. S. Boutros, and J. Barone
Philips Research, Briarcliff Manor, New York 10510

(Received 31 March 1997; accepted for publication 14 May 1997)

Tungsten films, grown by plasma-enhanced chemical vapor deposition for very large scale integration interconnect applications, suffer from a high internal tensile stress that leads to contact failure. We show with wafer curvature measurements that the stress can be relaxed via viscous flow at room temperature by irradiating the films with energetic ions after deposition. Transmission electron microscopy does not indicate significant structural changes in the W films during irradiation. We varied the irradiation conditions (from 140 keV B ions to 400 keV P ions) and find that the flow rate scales with the nuclear stopping power. Similarities and differences with beam-induced mixing and diffusion are discussed. © *1997 American Institute of Physics.* [S0003-6951(97)04428-8]

Tungsten thin films are an alternative solution for a low resistivity ohmic contact to silicon. Chemical vapor deposition (CVD) or plasma-enhanced CVD (PE-CVD) are among the commonly used techniques to fabricate these W films.[1,2] A drawback of these techniques is that the resulting W films often experience internal mechanical stress that may result in contact failure and reduction in yield. Developing a technique to reduce the internal stress in these films will result in an improvement of reliability.

Ion beam assisted deposition, using ion energies of several hundreds eV, has been used in an attempt to produce such low-stress metal films.[3,4] The success of this technique has been limited, since an intrinsic stress scaling law seems to exist caused by *atomic peening*, where an excess of interstitial atoms result in compressive stress.[5,6] In the present letter, we report the use of ions at several hundreds keV energy to relax the stress in W films after deposition is completed. This is an *ex situ* bulk treatment, rather than an *in situ* surface treatment. Ion irradiations in the keV and MeV energy regime have been shown to induce plastic deformation in amorphous covalent materials.[7,8] Stress relaxation occured via Newtonian viscous flow. The same apparent behavior was found for stress relaxation of Al films on SiO_2.[7]

We now show that intrinsic tensile stress in polycrystalline W films decreases exponentially during ion irradiation at room temperature. The relaxation rate is proportional to the nuclear stopping, indicating that relaxation is activated by ballistic interactions in the film. Structural changes upon stress relief are assessed by transmission electron miscroscopy (TEM). Comparison with other data on radiation-induced flow suggests that this is a universal phenomenon.

The W films were deposited on 4-in.-diam quartz wafers (525 μm thick), on which a 5% TiW adhesion layer has first been sputtered. During PE-CVD of W, via H_2 reduction of WF_6, the substrates were held at 360 °C. Figure 1(a) shows a dark-field cross-sectional TEM micrograph, obtained with a Philips EM430 microscope operated at 300 kV, of the layers after deposition. The W and TiW layers can clearly be distinguished in the image. The thickness of the TiW layer is 0.13 μm; the average thickness of the W film is 0.34 μm. The layers consist of textured columns; under a certain diffraction condition only a few columns light up in this dark-field image. The typical diameter of the columns in the W film ranges from 50 to 150 nm, as determined by plan-view TEM.

The wafer curvature was measured before and after the W deposition, using a laser deflection apparatus (Flexus F2418). The amount of wafer bending caused by the W deposition (measured from the edge to the center of the wafer) was typically about 25 μm. From this measurement, the integrated in-plane stress in the W film can be derived using the biaxial elastic modulus ($Y_{SiO_2}=1\times10^{11}$ Pa) and the thickness and diameter of the substrate.[9] The integrated tensile stress in our W films at room temperature was about 88 ± 9 N/m, which corresponds to an *average* local stress of $\sigma=(2.6\pm0.3)\times10^8$ Pa.

The tungsten layers were then irradiated with 400 keV P, 200 keV N, or 140 keV B ions. These energies were chosen such that the range plus the ion straggle[10] were about equal for each ion and corresponded to 80% of the thickness of the

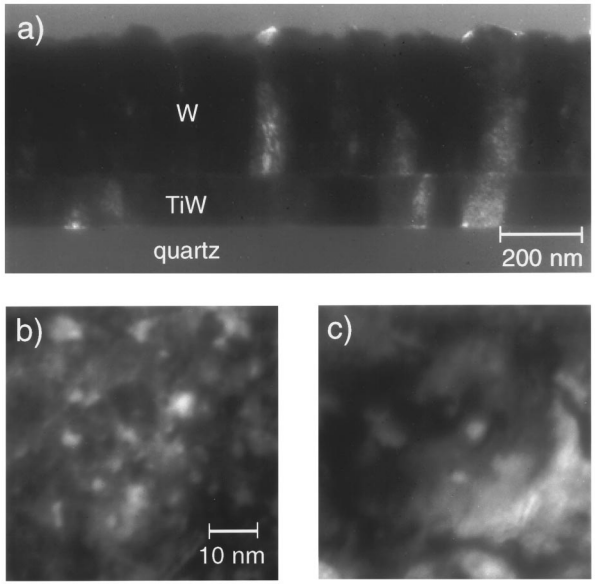

FIG. 1. Dark-field cross-sectional TEM micrographs of W films (a) and (b) before irradiation and (c) after irradiation with 400 keV P to a fluence of $2.5\times10^{14}/cm^2$.

[a]Electronic mail: snoeks@amolf.nl

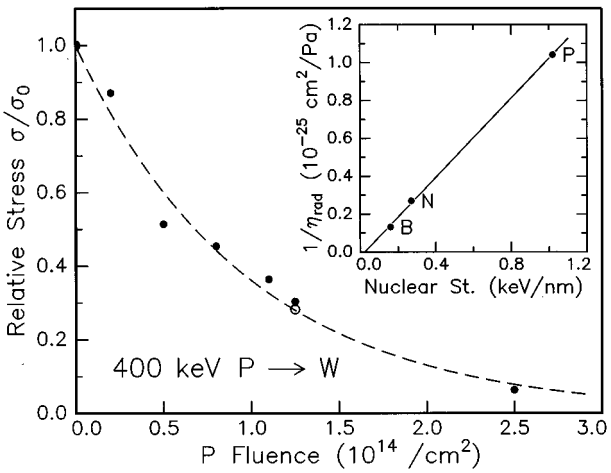

FIG. 2. Relative stress in the W film as a function of P fluence, measured *ex situ* in one film after subsequent irradiations at 400 keV. The initial stress in the film was about 2.6×10^8 Pa tensile. The dashed line is the best exponential fit. The inset shows the radiation-induced fluidity ($1/\eta_{rad}$) of W vs nuclear stopping power. Data are shown for P, N, and B irradiations, as indicated. The line shows the best linear fit to the data.

film. The ion beam current was held below 50 nA/cm^2 to keep the subtrates at room temperature. At specified ion fluences, the wafer was taken out of the implanter in order to measure the wafer curvature, after which it was reloaded in the implanter for the irradiation to be resumed.

Figure 2 shows the normalized stress in the W film measured on one single wafer as a function of P irradiation fluence. The y axis is normalized to the value found for the as-deposited wafer. The data show an exponential decrease of the stress in the W with P fluence. After a fluence of 2.5×10^{14}/cm^2 (corresponding to about 0.6 displacements per atom),[10] the stress is relaxed to less than 10% of the original value. Thermally activated creep processes at room temperature are many orders of magnitude slower than the creep rates observed in this ion beam experiment. The experiment was also performed with N and B irradiations. The stress was found to decrease exponentially in both cases, similar to Fig. 2, with the difference that factors of 3.9 and 8.0 higher ion fluences were needed, respectively, to reach the same amount of stress relaxation as shown for P.

There are several possible contributions to in-plane stress changes during irradiation, such as density changes, or plastic shear deformation. The latter may be characterized in terms of a radiation-induced viscosity,[7,8] if the strain rate is proportional to the stress (Newtonian shear flow) which is indeed the case in Fig. 2. Since the observed stress change is fully beam related, time is replaced by ion fluence, as was explained in Refs. 7 or 8. Following these references the general biaxial stress rate equation is given by

$$\frac{d\sigma}{d\phi}=Y_W\zeta(\phi)-\frac{Y_W}{6\,\eta_{rad}}\,\sigma, \tag{1}$$

where ϕ is the ion fluence, Y_W is the biaxial elastic modulus of poly crystalline tungsten, and η_{rad} the radiation-induced viscosity; ζ denotes the sum of strain rates due to phenomenalike density changes, and may depend on fluence.

If we assume that $\zeta=0$ (i.e., no density changes), the data from Fig. 2 can be used to estimate the radiation-induced viscosity. The solution of Eq. (1) in that case is a single exponential function

$$\frac{\sigma(\phi)}{\sigma_0}=\exp\left(-\frac{Y_W}{6\,\eta_{rad}}\,\phi\right), \tag{2}$$

where $\sigma(\phi)/\sigma_0$ is the normalized stress after irradiation to fluence ϕ, as depicted in Fig. 2. The dashed curve is the best fit of Eq. (2) to the data. Using $Y_W=57\times10^{10}$ Pa,[11] we find that η_{rad} of W under P irradiation is $(0.96\pm0.21)\times10^{25}$ Pa ions/cm^2, $(3.7\pm0.7)\times10^{25}$ Pa ions/cm^2 under N irradiation, and $(7.7\pm0.7)\times10^{25}$ Pa ions/cm^2 for B irradiated W. Hence, the fluence needed for relaxation increases with decreasing ion mass. This is summarized in the inset in Fig. 2, where the fluidity (inverse of the experimentally determined η_{rad}) is plotted against the maximum nuclear stopping power in the W film.[10] As can be seen, $1/\eta_{rad}$ is close to linearly proportional to the nuclear stopping power. For the range of ions and energies used, the electronic stopping power varied much less (from 1.3 keV/nm for 400 keV P to 0.66 keV/nm for 140 keV B) than the nuclear stopping power. We therefore conclude that electronic stopping contributes much less to the radiation-induced flow process than nuclear stopping.

After the P irradiations were completed, the layer was characterized by TEM. The film still consisted of the 50–150-nm-diam columnar structure, as was observed in Fig. 1(a) before irradiation. On smaller length scales, only minor changes were observed. Figure 1(b) shows a dark-field image taken in cross section within a column before irradiation, and Fig. 1(c) after irradiation with the same magnification. In Fig. 1(b), some very small ($\sim$3 nm) bright reflecting features are seen, which could be defect loops or small crystalline inclusions or grains. These features are only observed under specific orientations of the sample. These small bright features could no longer be observed within the columns after irradiation, as is illustrated in Fig. 1(c). Extended defects (such as dislocations, which may form as a result of stress relaxation) were not observed either.

Since the structural changes are only very minor, we conclude that the mechanism for stress relaxation is related to the point defects within the ion cascade. From that point of view, the atomic motion is a result of the defect density and temperature which increase very briefly and strongly within a few nm from where an energetic ion penetrates through the material. The temperature in the collision cascade may rise many thousands of degrees for a few picoseconds, sufficient to cause permanent rearrangement of the atoms.[12,13] This is known to lead to beam-induced mixing and diffusion, of which the rate scales with nuclear energy deposition if cascades or subcascades do not overlap.[12,14–16] When a stress field is present in the film, the atomic rearrangement will be biased such that the elastically stored energy in the film is lowered. Radiation-induced flow thus seems to be related to beam-induced diffusion.

Based on conceptual similarities and differences between diffusion and plastic flow,[8,17,18] it is perhaps possible to modify well established models for beam-induced diffusion[14–16] in order to describe beam-induced flow. One

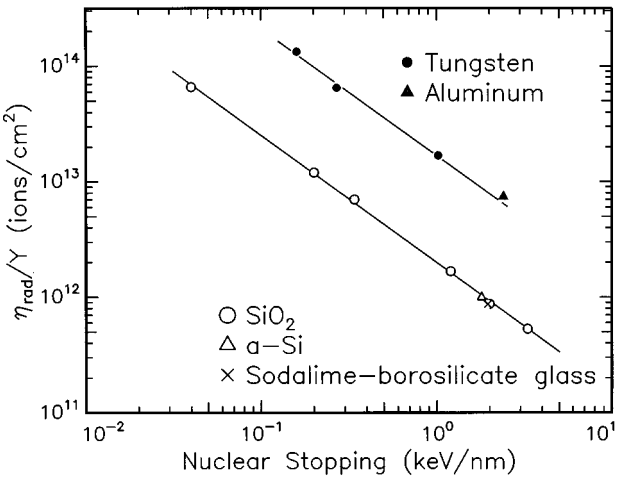

FIG. 3. Double log plot of η_{rad}/Y against nuclear stopping power for W (data from this work), Al (data from Ref. 7), SiO_2 (Ref. 8), sodalime-borosilicate glass (Ref. 8), and amorphous silicon (Ref. 7). The lines are best fits, and both have identical slopes of -1.1.

aspect that has to be taken into account in the case of plastic flow is how well a material can elastically accommodate an imposed mechanical strain. To test this idea, we plotted η_{rad} devided by the bielastic constant of the film for different materials in Fig. 3 as a function of maximum nuclear stopping power.[19] The data points for W (dots) are based on the present work, while the data points for annealed Al (black triangle) and pure amorphous silicon (open triangle) are based on measurements by Volkert and Polman,[7] and the data for SiO_2 (circles) and sodalime-borosilicate glass ($\times$) are obtained from Ref. 8. Although η_{rad} may differ widely from material to material, scaling by the biaxial elastic constant Y, results in a quantity that is a clear function of nuclear stopping for the polycrystalline metal films (filled data points) as well as the amorphous covalent films (open data points). On the log–log plot, the slopes of the best linear fits are -1.1 for both classes of materials, which approximately corresponds to an inverse relationship between η_{rad} and the nuclear stopping. This striking similarity in the behavior of different materials may indicate that the ion beam induced relaxation mechanism can be understood in a general theoretical framework, as has been the case for beam-induced diffusion.[14–16]

However, more work is needed to understand which other materials constants should be taken into account. For instance, the relaxation rate in the amorphous covalent materials is faster than the metals for the same amount of nuclear stopping. This might be a result of the recrystallization process which happens during the cooling phase of the collision cascade in the case of metals and not in the case of amorphous materials. For metals this means that although the stress may be fully relieved during the peak of the spike, some stress is reintroduced by the crystallization. This effectively results in a higher value for the radiation-induced viscosity. In glasses this is not the case since the cooling down does not cause a phase change inside the spike.[20]

It is outlined in, for example, Refs. 14–16 that beam-induced diffusion is composed of a (beam-induced) athermal contribution and a (beam-assisted) thermal migration. The beam-induced diffusivity scales linearly with nuclear stopping power in the athermal regime only, i.e., at irradiation temperatures below the transition temperature T_c. Brongersma *et al.*[20] have shown that the temperature dependence of η_{rad} in SiO_2, very similarly, shows a temperature dependent and independent regime with $T_c \approx 300$ K.[20] T_c is a materials parameter which scales with the cohesive energy.[15,16] Using a cohesive energy of 8.7 eV,[17] we find that for tungsten $T_c \approx 830$ K. Because this is well above room temperature, it is expected that our measurements of η_{rad} in W films were performed in the temperature-independent regime. To experimentally study the temperature dependence would be an interesting next step towards understanding radiation-induced flow of W.

In conclusion, the intrinsic stress in PE-CVD W films can be relaxed at room temperature by ion irradiation. The stress relaxes via creep or flow in an exponential fashion with ion fluence. The relaxation rate scales linearly with the portion of the stopping that is deposited into atomic collisions. This is consistent with the idea that the relaxation phenomenon is a ballistic effect, that will occur during irradiation with any ion. Based on conceptual similarities with beam-induced diffusion, we speculate that the product of beam-induced viscosity and diffusivity is a constant that depends on materials parameters such as the elastic constant and others.

The authors thank J. Burke for assistance with the ion irradiations. The TiW adhesion layers were grown by J. Murphy. Thanks are also due to R. Egloff, M. L. Brongersma, and A. Polman (FOM-Institute, Amsterdam, The Netherlands) for valuable discussions.

[1] E. K. Broadbent, J. Vac. Sci. Technol. B **5**, 1661 (1987).
[2] A. J. Learn and D. W. Foster, J. Appl. Phys. **58**, 2001 (1985).
[3] R. A. Roy, R. Petkie, and A. Boulding, J. Mater. Res. **6**, 80 (1991).
[4] R. A. Hoffman, J. C. Lin, and J. P. Chambers, Thin Solid Films **206**, 230 (1991).
[5] H. Windischmann, J. Appl. Phys. **62**, 1800 (1987).
[6] C. A. Davis, Thin Solid Films **226**, 30 (1993).
[7] C. A. Volkert and A. Polman, Mater. Res. Soc. Symp. Proc. **235**, 3 (1992).
[8] E. Snoeks, T. Weber, A. Cacciato, and A. Polman, J. Appl. Phys. **78**, 4723 (1995).
[9] G. G. Stoney, Proc. R. Soc. London Ser. A **82**, 172 (1909).
[10] TRIM-89: J. P. Biersack and L. J. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).
[11] S. W. H. Yih and C. T. Wang, *Tungsten* (Plenum, New York, 1979).
[12] T. Diaz de la Rubia, R. S. Averback, Horngming Hsieh, and R. Benedek, J. Mater. Res. **4**, 579 (1989).
[13] M. Ghaly and R. S. Averback, Phys. Rev. Lett. **72**, 364 (1994).
[14] W. Bolse, Mater. Sci. Eng. **12**, 53 (1994).
[15] Y.-T. Cheng, Mater. Sci. Rep. **5**, 45 (1990).
[16] M. Nastasi and J. W. Mayer, Mater. Sci. Eng. R. Rep. **12**, 1 (1994).
[17] P. A. Egelstaff, *An Introduction to the Liquid State* (Oxford University Press, Oxford, 1992), Chap. 13.
[18] P. A. Duine, J. Sietsma, and A. van den Beukel, Phys. Rev. B **48**, 6957 (1993).
[19] The average stopping power in the film is about 75% of the maximum stopping power for all present irradiations.
[20] M. L. Brongersma, E. Snoeks, and A. Polman (unpublished).