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Tensile crack patterns in Mo/Si multilayers on Si substrates under high-temperature bending

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ABSTRACT Mo/Si multilayers with a single-layer thickness in the nanometre range (60 Mo/Si layers in total) were deposited on Si(100) substrates by dc magnetron sputtering. Upon uniaxial bending at elevated temperatures between 300 and 440 °C in vacuum, unconventional crack patterns formed in the multilayers. Tensile stress within the multilayer stack and Si substrate due to bending during thermal treatment was estimated to be on the order of 100 MPa. A combination of external bending, residual and thermal stresses is considered to be the reason for this phenomenon. Cracks had either a sinusoidal or a spiral shape. The surface frequency of the spirals observed was $\sim 10\,\mathrm{cm}^{-2}$, with a track width of $\sim 30\,\mu\mathrm{m}$ and a spiral diameter of $\sim 300\,\mu\mathrm{m}$. In general, cracking was accompanied by complete local de-bonding of the whole Mo/Si multilayer stack from the substrate. Fracture patterns were studied by optical microscopy. In addition, the morphological parameters of the remaining non-delaminated multilayers were determined by means of X-ray reflectometry supported by investigation of phase content by wide-angle X-ray scattering.

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Multilayers are widely used for various technological applications. For example, Mo/Si multilayers are used as X-ray and EUV (extreme ultraviolet) mirrors. Thermal stability of multilayers with a typical layer thickness on the order of a nanometre is an important feature for their applicability in modern technology. It is well known that the stress state can influence the thermal stability. Apart from a direct mechanical destruction of the layers (cracking, de-bonding from substrates, etc.), stored elastic energy due to residual stress in addition to thermal energy contributions can drive structural changes. Thus, under the influence of mechanical stresses, the structural phase formation within nanolayers can be observed at significantly lower temperatures [1] and thermally induced changes of the morphological layer structure can be strengthened [2].

While the intrinsic residual stress is essential for the use of optics on non-curved substrates, bending steps are often intended technologically after layer deposition for creation of imaging or adaptive optics.

It is desired to produce devices that are stable over a long-term period of service. On the other hand, there is a still growing field of thin-film self-assembly with typical dimensions in the micrometre range. While lithographic methods are important, apart from aspects of cost reduction, self-organised structuring processes can allow new and unique applications.

It is the aim of the present communication to report on a self-assembly process of structuring by unconventional crack formation at high-temperature bending of Mo/Si multilayers on a Si substrate, which might be interesting from both points of view mentioned above.

Mo/Si multilayers of 60 periods were grown on Si(100) substrates to a 500-µm total thickness by dc magnetron sputtering (0.1 Pa Ar pressure). The substrate was held at room temperature during deposition at a 65-mm distance from the target. Molybdenum was deposited first on a sub-nm-range rms roughness Si substrate with a ∼ 2.5-nm-thick natural SiO_2 layer. The average thickness of the single layers was determined by X-ray reflectometry to be $d_{\mathrm{Mo}} = (1.9 \pm 0.1)$ nm for the Mo layers and $d_{\mathrm{Si}} = (3.2 \pm 0.1)$ nm for the silicon layers.

Wide-angle X-ray scattering (WAXS) indicated that the Si layers were amorphous after deposition, while the Mo layers exhibited a distorted long-range translation order (W-structure type). Annealing above $\sim 300\,°\mathrm{C}$ led to silicide formation, which was almost unaffected by the stressed state in the context of our investigation accuracy. However, the influence of a general process of silicide formation at the multilayer interfaces on the cracking phenomenon reported here should not be excluded. This is encouraged by the fact that Mo/Si multilayers with C and B_4C barrier layers at the interfaces, which hinder the interdiffusion of Mo

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and Si and thereby the formation of silicides [3], did not exhibit the behaviour reported here.

Samples were subjected to ramping thermal treatment in a tubular furnace at temperatures between 300 °C and 440 °C under vacuum ($p < 4 \times 10^{-4}$ Pa), both with and without the influence of external mechanical force. Annealing time per step (or temperature stage) was 20 min, as in Fig. 1, where annealing regimes are visualised.

The silicon substrate and the adherent multilayer stack were bent, putting the multilayer in tension during annealing. In order to achieve this, samples (silicon strips 20-mm long and 8-mm wide) were placed onto two ruby crystal prisms in contact with the multilayer side (see Fig. 2). A third ruby crystal prism transferred the load to the samples by means of mechanical contact to the middle of the back silicon side of the samples. Altogether this led to uniaxial tension within the multilayer transverse to the applied force (horizontal direction in Fig. 2). A sign reversal of external load (compressive stress within the multilayer) led to the silicon substrate breaking at temperatures above ~ 400 °C.

Based on quantitative values of applied force, film thickness, Young's modulus, substrate thickness and sample size, the induced stress was estimated to be in the order of 100 MPa. In particular, using elastic constants given in [4], the Young's modulus for a Si(100) substrate was calculated to be about to 130 GPa.

After each annealing step (see Fig. 1), the samples were subjected to investigation by means of optical microscopy, X-ray reflectometry and WAXS at ambient conditions and room temperature. The phenomenon reported here was observed after the last annealing at 440 °C and high tensile stress within the multilayer exclusively. Due to the extraordinary surface frequency of cracks and de-bonding, continuation of the investigation at higher temperatures was impossible. From X-ray reflectometry carried out for samples annealed at 400 °C, it was determined that at this stage multilayers exhibited significant interdiffusion at the Mo/Si interfaces; however, layers were not homogenised.

Figures 3–5 show typical optical micrographs of the crack patterns. Two characteristic groups of the cracking behaviour are emphasised: sinusoidal crack structures and regular spirals. The surface frequency of the spirals observed was $\sim 10\,\mathrm{cm}^{-2}$, with a track width of ~ 30 μm and ~ 300-μm spiral diameter. In general, cracking is accompanied by de-bonding of the areas adjacent to through-thickness cracks. Similar spiral objects (several hundred micrometres to a few millimetres in diameter) were found on fragments of thin layers of drying precipitates [5]. The reason for these crack patterns was meant to arise from an unusual (tensile) stress-relaxation process governed by the fold-up and de-bonding of the fragments from the substrate.

We believe that the crack oscillations here, either spiral or sinusoidal, are due to the interaction of the crack-tip stress field with the biaxial residual stress, similar to the phone cord buckling delamination observed in thin films under compressive residual stress [6]. This can be recognised from an example of the structures shown in Fig. 5.

These results and a detailed theoretical discussion of the phenomenon

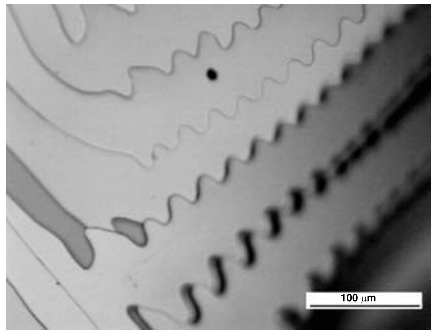

FIGURE 3 Optical micrograph of the relaxed surface showing oscillating crack patterns

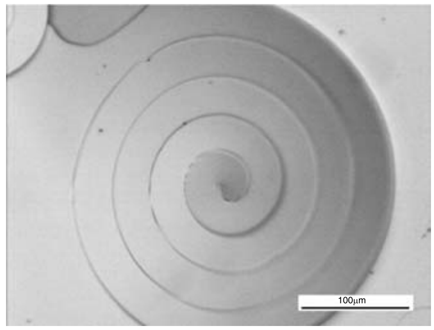

FIGURE 4 Typical optical micrograph of the relaxed surface showing cracks forming regular spirals

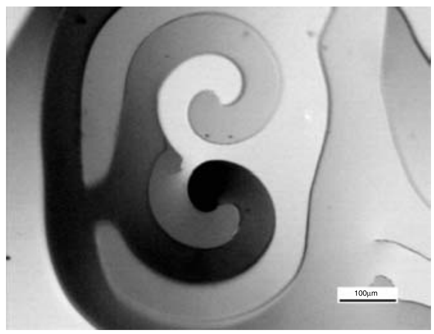

FIGURE 5 Optical micrograph of the relaxed surface showing cracks forming interconnected regular spirals

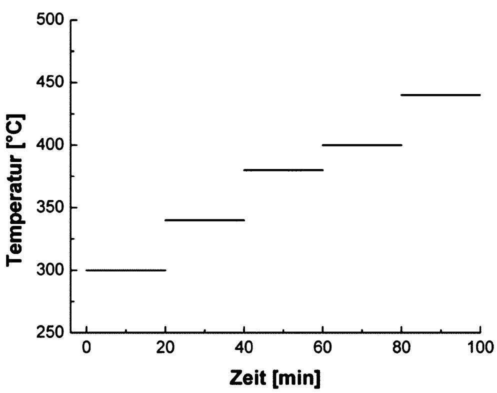

FIGURE 1 Temperature vs. annealing time for sample treatment. After deposition for 20 min at a given temperature and cooling in vacuum, samples were subjected to investigation by means of optical microscopy, X-ray reflectometry and WAXS at ambient conditions and room temperature

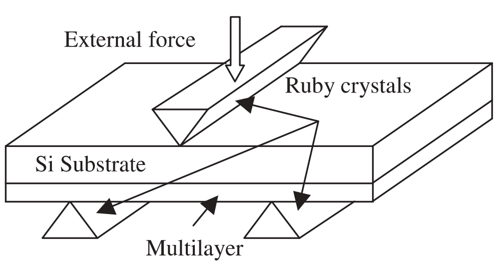

FIGURE 2 Three-point-bending set-up schematics

will be the subject of a further detailed publication [7].

Here we want to communicate that the process of crack-pattern formation is reproducible. The spirals presented here are candidates for micromechanical applications as springs, etc. and, coupled with different kinds of physical fields, also for applications in sensor technology.

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REFERENCES

1 S.L. Chen, H.M. Lo, L.W. Cheng, S.M. Chang, L.J. Chen: Thin Solid Films **424**, 33 (2003)

2 D.C. Meyer, A. Klingner, T. Leisegang, T. Holz, R. Dietsch, P. Paufler: Mat. Res. Soc. Symp. Proc. **695**, L12.21 (2002)

3 T. Böttger, D.C. Meyer, P. Paufler, S. Braun, M. Moss, H. Mai, E. Beyer: Thin Solid Films (2003) (in the press)

4 P. Paufler: *Physikalische Kristallographie* (Akademie, Berlin 1986)

5 Z. Néda, K.-T. Leung, L. Józsa, M. Ravasz: Phys. Rev. Lett. **88**, 095 502 (2002)

6 A.A. Volinsky: Mat. Res. Soc. Symp. Proc. **749**, W10.7 (2002)

7 A.A. Volinsky, D.C. Meyer, T. Leisegang, P. Paufler: in *Fall 2003 MRS Symposium U: Thin Films – Stresses and Mechanical Properties X* (to be published)