Appl. Phys. A 69 [Suppl.], S455–S457 (1999) / Digital Object Identifier (DOI) 10.1007/s003399900262

Applied Physics A
Materials
Science & Processing

Study of laser-deposited metallic thin films by a combination of high-resolution ex situ and time-resolved in situ experiments

M. Störmer[1,*], K. Sturm[1], S. Fähler[1,], M. Weisheit[1], J. Winkler[1], S. Kahl[1], Ph. Kesten[1], A. Pundt[1], M. Seibt[2], S. Senz[3], H.-U. Krebs[1]**

[1] Institut für Materialphysik, Universität Göttingen, Hospitalstraße 3–7, 37073 Göttingen and SFB 345, Germany
(Fax: +49-551/507-1750, E-mail: krebs@umpsun1.gwdg.de)
[2] IV. Physikalisches Institut, Universität Göttingen, Bunsenstraße 13–15, 37073 Göttingen, Germany
[3] MPI für Mikrostrukturphysik, Weinberg 2, 06120 Halle/Saale, Germany

Received: 21 July 1999/Accepted: 11 September 1999/Published online: 22 December 1999

Abstract. Laser-deposited metallic alloys and multilayers were studied in detail by a combination of high-resolution ex situ and time-resolved in situ experiments. The purpose of these experiments is to better understand the special properties of laser-deposited metallic films in comparison with conventionally prepared thin films. During deposition, thickness, resistance, and electron diffraction (THEED) experiments show that the film surface is resputtered, local mixing at the interfaces of multilayers on a nanometre scale occurs, and metastable phases up to large film thicknesses are formed. After deposition, a compressive stress of 1–2 GPa was measured using four-circle diffractometry, and growth defects were observed on an atomic scale by electron microscopy (HRTEM) and field ion microscopy (FIM). The obtained structural details of the metallic films can be explained by an *implantation model* for the laser deposition process.

PACS: 68.55.-a

As was found earlier, metallic films grown by pulsed laser deposition (PLD) differ in many ways from sputtered or evaporated thin films [1, 2]. Often, metastable phases with large supersaturations are formed, lattice parameters are enlarged, and mixing at the interfaces of multilayers occurs. It was determined that the occurrence of ions with kinetic energies of around 100 eV [3, 4] was responsible for this [2]. The purpose of our current study is to investigate and better understand the mechanisms leading to the special properties of laser-deposited metallic alloys and multilayers in comparison with conventionally prepared thin films. Therefore, laser deposited metallic alloys and multilayers were studied in detail by a combination of time-resolved in situ and high-resolution ex situ experiments.

*Current address: GKSS Geesthacht, Max Planck Str., 21502 Geesthacht, Germany
**Current address: IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

COLA'99 – 5th International Conference on Laser Ablation, July 19–23, 1999 in Göttingen, Germany

1 Experimental

About 300 nanometre-thick metallic binary alloys and multilayers were deposited by PLD at room temperature in a UHV chamber (base pressure 10^{-9} mbar) from metallic elementary foils using a KrF excimer laser (LPX110i by Lambda Physics, 8 J/cm^2 laser fluence, 248 nm wavelength, 30 ns pulse duration). The atoms and ions ablated from the targets were deposited on Si and Al_2O_3 substrates with a target-to-substrate distance of about 3–5 cm. The average film composition and single-layer thicknesses of the multilayers were determined by the number of pulses on each target as described in [5]. Stress measurements were performed using a four-circle diffractometer (Philips X'Pert MRD). On selected samples, high-resolution transmission electron microscopy (HRTEM, Philips CM200) was performed. Some films deposited on W tips were analysed with atomic resolution by field ion microscopy (FIM). During film growth, a quartz microbalance (Leybold Inficon XTM/2) was used to determine the deposited mass. Resistance measurements were done in situ using a four-point method, and high energy electron diffraction experiments were performed in a transmission geometry (THEED) at an incident angle of 3–4° and an energy of 25 kV.

2 High resolution ex situ experiments

As was shown earlier [1, 6, 7], X-ray diffraction patterns indicate that the lattice parameters of all laser-deposited alloys are strongly enlarged in the growth direction.

From X-ray stress measurements [1] (not shown here) performed under different tilt angles ψ, it is observed that the lattice spacings decrease with increasing ψ and follow a $\sin^2\psi$ dependence. It can be concluded that the lattice expansion is partially due to the *high compressive stress* of 1–2 GPa in PLD films. An additional enlargement of the stress-free lattice parameters exists, indicating that there are defects in the films, as proposed in [6].

High-resolution measurements show that *a large number of defects* are observed in laser-deposited metallic films.

HRTEM investigations in cross-section give clear evidence for different types of structural defects. In Fig. 1, the HRTEM image of a pure Fe film on Si is shown. As is typical also for other samples, many dislocations become visible on (110) planes. They are probably formed during a partial release of the high compressive stress. To determine the dislocation density of such films, the images of Fe, Fe-Ag, and Pd-Nb films were Bragg-filtered, indicating an unusually high dislocation density of up to about 10^{12} /cm^2. Additionally, columnar growth (not shown here) with a typical column diameter of about 20 nm is observed in supersaturated Fe-Ag samples.

For the FIM measurements, about 80 nanometre-thick metallic films were deposited on W tips. In the FIM images, grain boundaries, dislocations, and point defects can directly be observed with an atomic resolution, again indicating that many defects occur in laser-deposited films. In Fig. 2, details of the microstructure of a Pd layer in a Pd/Nb multilayer are shown: a grain boundary, a screw dislocation, and point defects (probably vacancies) are marked. Other FIM experiments show that *atoms are implanted* about 1–2 nm deep into the W tip during PLD.

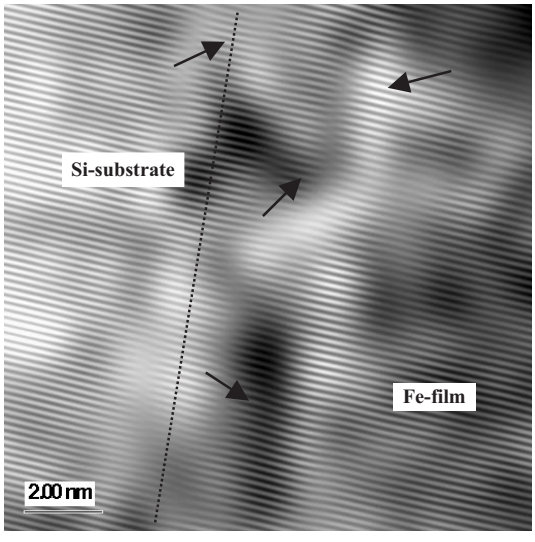

Fig. 1. High-resolution transmission electron microscope image of an Fe/Si interface (*dotted*) in cross-section after Bragg filtering. Some dislocations are marked by *arrows*

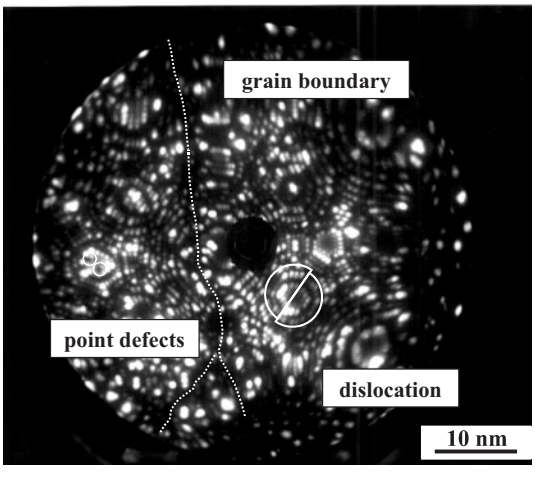

Fig. 2. Field ion microscope (FIM) image with atomic resolution of the Pd layer in a Pd/Nb multilayer, deposited by PLD on a W tip. Point defects, a screw dislocation, and grain boundaries are marked

3 Time-resolved in situ experiments

In order to gain a detailed insight into the growth process, different in situ experiments were done after each laser pulse during deposition.

In situ THEED measurements, performed for Fe/Ag, Cu/Ag, and Co/Cr, indicate the *formation of metastable phases* at the interfaces of multilayers (for details of our THEED technique see [8]). From the electron diffraction patterns, the intensities along given lines are determined and plotted versus deposition time. In Fig. 3, the results are shown for Co/Cr multilayers epitaxially grown on Ag (deposited on Si) at room temperature. At the Ag/Cr interface, Cr stays fcc and then transforms into the equilibrium bcc structure, which is reached after 2 nm. At the Cr/Co and Co/Cr interfaces, the metastable bcc and fcc phases, respectively, remain even over a larger thickness, before the transformation into the corresponding equilibrium phases is completed, which occurs after about 4 nm. Therefore, the metastable phases are formed over larger thicknesses than during preparation with conventional deposition techniques like sputtering or evaporation. This is a hint that intermixing effects occur at the interfaces.

The in situ resistance measurements give further indications of an *intermixing* of the layers. In the case of the Zr/Fe multilayers (Fig. 4), the conductance increases only slightly, when Fe is first deposited on Zr. This can be explained by the formation of an amorphous phase at the Zr/Fe interface over a thickness of about 7 nm. This thickness of the amorphous interlayer is much larger than that observed in the case of sputtered Zr/Fe multilayers, where only a 1.5-nm-thick amorphous interlayer was found [9]. This shows again the influence of intermixing in addition to the thermodynamically induced amorphization reaction.

In situ measurements of the deposition rate show that *resputtering* also occurs during PLD. In the case of the deposition of Si on Au, the mass drops slightly at first, before increasing again (see Fig. 5). Obviously, Au is resputtered by the Si ions. Similar experiments show that during PLD, the effective sputter yield for Ag is about 0.55 at 5 J/cm^2 [10]. This means that less than half of the ablated material reaching the substrate is actually deposited on the film surface.

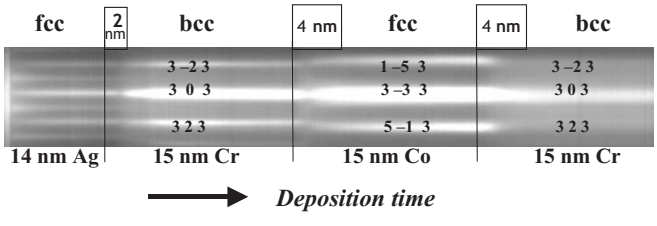

Fig. 3. Time evolution of the positions and intensities of the reflections along a selected line in the THEED measurements during deposition of an Ag/Cr/Co/Cr film on Si(111). The formation ranges of the metastable phases at the interfaces are marked

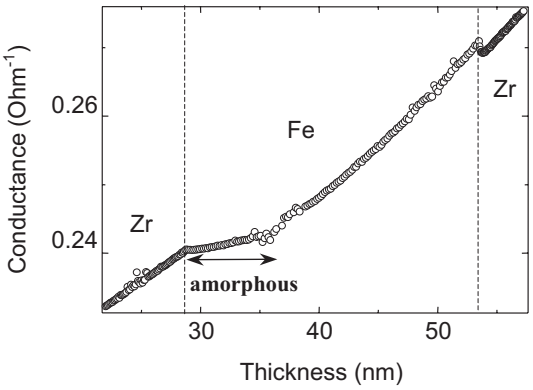

Fig. 4. Part of an in situ conductance measurement of an Fe/Zr multilayer during deposition. While depositing Fe onto Zr, an amorphous phase of about 7-nm thickness is formed at the Fe/Zr interface

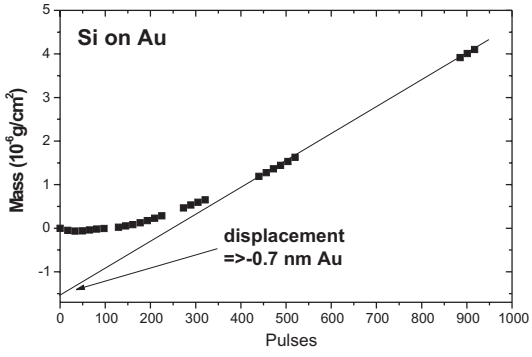

Fig. 5. Part of the in situ measurements of the mass deposited during PLD of an Si/Au multilayer. When depositing Si onto Au, the mass stays almost constant at first, indicating resputtering of Au. The extrapolated displacement corresponds to a resputtered Au layer of 0.7-nm thickness

4 Implantation model

All these experiments can be understood in terms of the following *implantation model* (see Fig. 6): As is well known, atoms are deposited onto the film surface with a kinetic energy of about 5–10 eV during PLD. At a laser fluence of 8 J/cm^2, at least 50% of the deposited particles are ions, which possess kinetic energies in the range of 100 eV [3, 4]. The kinetic energy of the ions lies well above the displacement threshold of bulk atoms, which is in the order of 15–25 eV for most metals [11]. Therefore, surface atoms of the film are *resputtered* and the energetic ions are *implanted* below the film surface leading to ballistic displacements of atoms within the film, the formation of defects, and gradual changes of the concentration across layer interfaces.

5 Conclusions

The above implantation model explains the performed experiments and describes the influence of the energetic ions on the growth process and the formation of defects. While the rate measurements directly show the resputtering effect

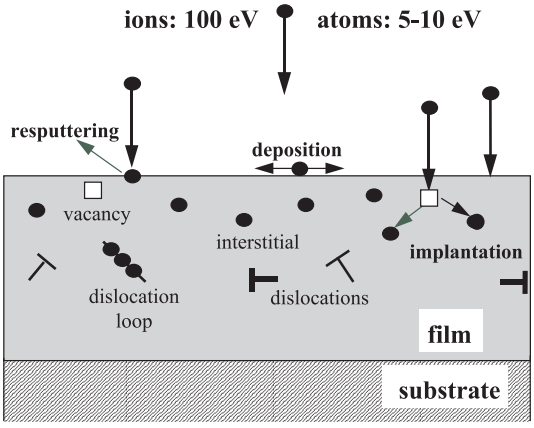

Fig. 6. Atomic processes occurring during laser deposition of the ablated particles in ultrahigh vacuum. While the atoms are deposited on the film surface, the energetic ions lead to resputtering and implantation below the film surface. Vacancies, interstitials, agglomerations of point defects, and a large number of dislocations are formed

of an approximately 1-nm-thick surface layer at the interfaces of multilayers, it can be concluded from these experiments [3] that the region of intermixing is about 1–2 nm. With FIM and HRTEM experiments, point defects, dislocations, and agglomerations of defects (e.g. dislocation loops) were directly observed. In the case of multilayers, intermixing, which is also induced by the energetic ions, is observed at the interfaces of multilayers by the resistance and THEED measurements. This intermixing is much stronger than during conventional deposition techniques and therefore leads to the formation of much thicker metastable phases (2–7 nm) at the interfaces of multilayers.

In summary, from the combination of our different experiments performed ex situ with a high-resolution and in situ during deposition, many details of the growth process of laser-deposited films under ultrahigh vacuum conditions can be understood in terms of resputtering and implantation effects induced by the ablated kinetic ions. The resputtering, implantation, and atomic mixing can be prevented by reducing the kinetic energy of the ablated particles, for instance, by the use of an inert gas atmosphere [10]. Indeed, by using an Ar gas pressure of 0.04 mbar during PLD, epitaxial multilayers with sharp interfaces have been grown.

References

1. M. Störmer, H.U. Krebs: J. Appl. Phys. **78**, 7080 (1995)
2. H.U. Krebs: Int. J. Non-Equilibrium Proc. **10**, 1 (1997)
3. J.G. Lunney: Appl. Surf. Sci. **86**, 79 (1995)
4. S. Fähler, H.U. Krebs: Appl. Surf. Sci. **96-98**, 61 (1996)
5. H.U. Krebs, O. Bremert: Appl. Phys. Lett. **62**, 2341 (1993)
6. H.U. Krebs, M. Störmer: Phys. Rev. Lett. **75**, 3966 (1995)
7. H.U. Krebs, M. Störmer, S. Fähler, O. Bremert, M. Hamp, A. Pundt, H. Teichler, W. Blum, T.H. Metzger: Appl. Surf. Sci. **109–110**, 563 (1997)
8. S. Fähler, M. Weisheit, H.U. Krebs: Mat. Res. Soc. Symp. Proc. **502**, 139 (1998)
9. C. Michaelsen, M. Piepenbring, H.U. Krebs: J. Phys. C **4**, 157 (1990)
10. K. Sturm, S. Fähler, H.U. Krebs: Appl. Surf. Sci., accepted
11. H. Ullmaier: MRS Bull. **22**, 14 (1997)