SURFACE ROUGHENING, COLUMNAR GROWTH AND INTRINSIC STRESS FORMATION IN AMORPHOUS CuTi FILMS

U. v. Hülsen *, P. Thiyagarajan **, U. Geyer *,

* 1. Physikalisches Institut and SFB 345, 37073 Göttingen, Germany

** Argonne National Laboratory, Argonne, IL 60439, USA

ANL/IPS/CP-92694
CONF-971201--
RECEIVED

AUG 26 1997

OSTI

ABSTRACT

The growth of amorphous CuTi films, prepared by electron beam evaporation, is investigated by Scanning Tunneling Microscopy (STM), Small Angle Neutron Scattering (SANS) and in situ measurements of intrinsic mechanical stresses (ISM). In early growth stages the films develop compressive stresses and, with increasing film thickness, a crossover to tensile stresses. In the same thickness range the STM investigations show a change in the growth mode. Our experiments suggest a transition from planar growth with statistical surface roughening to columnar growth.

INTRODUCTION

Many multicomponent metallic alloy films, especially prepared from transition metals by thermal evaporation in vacuo or sputtering, remain amorphous at substrate temperatures up to a few hundred degrees above room temperature [1-4]. Some amorphous binary and ternary metallic films can therefore be utilized as diffusion barriers for Cu metallization of Si devices, even up to 800°C [3, 5]. For their performance it seems to be crucial that these films are homogenous, without interfaces along which diffusion could take place, and free of intrinsic stresses. In addition, homogenous amorphous films should be perfect to test macroscopic growth models [6] because of their structural isotropy and homogeneity. In this paper we report a combination of intrinsic stress measurements, Scanning Tunneling Microscopy and Small Angle Neutron Scattering studies of thin amorphous metallic CuTi films in order to discuss the growth modes of these films.

EXPERIMENTAL

The Cu-Ti films were prepared in an ultrahigh-vacuum chamber by simultaneous condensation of the elementary metal vapors from two electron-beam evaporation sources onto 500 μm thick single-crystal quartz substrates or onto the amorphous SiO_2 layer of a naturally or thermally oxidized 500 μm thick Si(100) wafer. The results are independent of the substrates used. The growth rate of all films was 0.7 nm/s. The metal atoms arrived on the substrates at 23° from perpendicular. X-ray diffraction analysis of the films did not show contributions from crystalline phases to the diffraction patterns. The in-plane mechanical stresses were measured in situ during the condensation process by a cantilever beam technique using an optical two beam deflection method [7]. The film surfaces were investigated by scanning tunneling microscopy in the constant current mode. Scan sizes and vertical scales are given in the figure captions. SANS samples consisted of a stack of ten 50 μm thick Si(100) wafers, each with 300 nm thick CuTi films condensed onto both sides at $T_s = 300$ K. SANS measurements were carried out at the Intense Pulsed Neutron Source, Argonne National Laboratory, with a measured q-vector range of $0.05 \text{ nm}^{-1} < |q| < 2.5 \text{ nm}^{-1}$.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Fig.1. (a) Intrinsic stress measurements (ISM) of CuTi films of different compositions at room temperature. The average in-plane stress times the thickness is plotted vs. the film thickness t . The slope of the curves at thickness t gives the stress that is formed in the layer $t+\Delta t$. The $\text{Cu}_{50}\text{Ti}_{50}$ film has not reached a state of growth with saturated tensile stress.

(b) ISM of $\text{Cu}_{30}\text{Ti}_{70}$ condensed at room temperature. The dotted lines indicate the shutter operations. There is no stress formation when the shutter is closed

RESULTS

Fig. 1a shows the in situ stress measurements for different film compositions during growth at room temperature. In all curves we see a crossover from compressive to tensile stresses. The crossover thickness depends on the film composition: the higher the Cu content of the alloy, the higher is the crossover thickness. In the measurement of Fig 1b, the growth process was interrupted by drawing a shutter between substrate and evaporator at different growth stages. No further stress generation is observed after the shutter is closed in any growth stage. If we cut out the parts of the curve where the shutter was closed, we get the same intrinsic stress values as without interruption of the growth. Fig. 2 (a-c) show STM images of $\text{Cu}_{30}\text{Ti}_{70}$ condensed at substrate temperature $T_s = 300\text{K}$ at different growth stages. Fig. 2a shows the surface of the film in the compressive stress range, Fig. 2b in the crossover range, and Fig. 2c in the tensile range. The surface topography does not change with further growth. This evolution of surface topography is also found for $\text{Cu}_{40}\text{Ti}_{60}$ and $\text{Cu}_{50}\text{Ti}_{50}$. The crossover range in which the surface changes from relatively smooth to the sharply clustered surface always correlates with the crossover thickness of the stress measurements. The mean diameter of the clusters is about 20 nm for

Fig. 2. STM images of the surface of amorphous $\text{Cu}_{30}\text{Ti}_{70}$ films. (a) 100 nm thick, $T_s=300\text{K}$; (b) 150 nm thick, $T_s=300\text{K}$; (c) 250 nm thick, $T_s=300\text{K}$; (d) 300 nm thick, $T_s=400\text{K}$. The scan size is $500\text{ nm} \times 500\text{ nm}$ in all cases, the gray scale covers 15 nm in (a)-(c) and 25 nm in (d)

Fig 2c. The diameter increases with Cu content and with T_s . Fig. 2d shows an STM image of a 300 nm thick $\text{Cu}_{30}\text{Ti}_{70}$ film condensed at $T_s=400\text{K}$. The clusters have a mean diameter of 32 nm. In Fig. 3 we show a log-log plot of the rms surface roughness w of the films vs. film thickness t for different compositions in order to achieve the growth exponent [6]. The growth exponent is about 1/4 until the film reaches the crossover thickness. Then a dramatic change of the growth mode occurs as indicated by a growth exponent of about 4. Finally no further increase of w can be detected. Fig. 4 shows a log-log plot of w vs. lateral scan size L for the films at high thicknesses. For small lateral size, we find a roughness exponent of about 0.7 which can also derived from the height-height correlation function [6]. The surface roughness saturates at scansizes of about $L=40\text{nm}$.

Fig.3. Surface roughness (root mean square of surface height function) vs. film thickness for CuTi films of different compositions, condensed at room temperature. The black line is a linear fit of the roughness values of the $\text{Cu}_{40}\text{Ti}_{60}$ films with a slope of 0.25. The error bar plotted on the left side is typical.

Fig.4. Surface roughness vs. lateral scan size for CuTi films at high film thicknesses. The black line is a linear fit of the roughness values of the $\text{Cu}_{40}\text{Ti}_{60}$ film at small scan sizes with a slope of 0.7.

In Fig 5, SANS cross section data $S(q)$ of $\text{Cu}_{30}\text{Ti}_{70}$ and $\text{Cu}_{40}\text{Ti}_{60}$ are shown. They were measured at normal incidence of the neutron beam with respect to the film plane. The increase of the scattering cross section $S(q)$ with decreasing wavenumber q reveals the existence of inhomogeneities on a length scale of a few 10 nm in the films. We relate this scattering contrast to the cluster boundaries observed by STM and conclude that these extend into the film volume. The smaller overall $S(q)$ in (b) indicates a smaller volume fraction of boundaries in the $\text{Cu}_{40}\text{Ti}_{60}$ films.

In order to get further information on the geometry of the inhomogeneities in the films, 2D SANS diffraction patterns for oblique beam incidence were measured. While normal neutron beam incidence leads to isotropic scattering, the oblique incidence results in anisotropic patterns. In Fig. 6 the corresponding $S(q_x, q_y)$ data of $\text{Cu}_{30}\text{Ti}_{70}$ for normal (a) and 30° incidence (b) are given. The anisotropy in (b) shows that the clusters seen by STM at the surface extend deeper perpendicular to the film than in the film plane, consistent with a columnar microstructure.

Fig. 5. 1D-SANS cross section data $S(q)$ of 20×300 nm thick $\text{Cu}_{30}\text{Ti}_{70}$ films (a) and 20×300 nm thick $\text{Cu}_{40}\text{Ti}_{60}$ films (b). All films were deposited at $T_S=300\text{K}$. The cross section data are taken at normal beam incidence.

Fig. 6. 2D-SANS cross section data $S(q_x, q_y)$ of 20×300 nm thick $\text{Cu}_{30}\text{Ti}_{70}$ films ($T_S=300\text{K}$) measured at normal (a) and 30° oblique (b) beam incidence.

CONCLUSIONS

These results make the following growth behavior of the amorphous CuTi films likely. The arriving atoms are strongly bonded to the surface, and due to the low reduced temperature $T^*=T_S/T_M$ (T_M = melting temperature) there is only small surface diffusion before the next atomic layer is deposited.

The growth exponent obtained from the solution of a growth equation introduced independently by Wolf and Villain [8] and Das Sarma and Tamborenea [9] is $1/4$, which is in good agreement with our results below the crossover thickness. In this equation, the growth is described by two terms: the particle flux to the surface with statistical fluctuations and a surface diffusion term. Though this equation is introduced to describe MBE Experiments, the growth of an amorphous film should be an excellent system to test it because of the absence of diffusion barriers like monoatomic steps at the surface.

When the film reaches a critical roughness it begins to form boundaries between its hillocks. This is the start of the crossover that is observed in the stress measurements and the STM investigations. The roughening in the crossover range is not further driven by statistical fluctuations in the vapor flux but by the ratio of the surface and the interface energies which defines the equilibrium contact angle of two clusters [10]. Since this driving force is nonlocal, the roughening of the clusters cannot be described by continuous growth equations of the Wolf Villain type. The roughening is finished when this contact angle is reached. Due to the surface tension, the clusters have a spherical shape. With the formation of the cluster's boundaries, formation of tensile stress is connected as described by the mismatch model of Hoffman and discussed elsewhere [10-12].

The saturation of the rms-exponent with increasing L can be understood if we assume that the boundaries act as diffusion barriers, and so the lateral correlation propagation of the surface height function stops at these boundaries. The origin of the column diameter is found in the lateral correlation length of the surface described by the growth model for small film thickness [13]. This correlation length depends on the surface diffusion during the film growth. Therefore, the diameter increases with increasing substrate temperature as is shown in Fig. 2.

In summary, the combination of STM and SANS measurements reveals a change of growth mode in amorphous CuTi films from planar to columnar growth. This change can also explain the change in ISM to tensile stress. The initiation of the columnar growth can be described by statistical roughening of the surface. The growth exponent in that regime is in agreement with the growth equation of the Wolf Villain type in which surface diffusion plays the important role. After formation of the column boundaries has started, the roughening exponent increases dramatically and cannot be described by statistical roughening models. The ratio of surface energy to interface energy now determines the equilibrium contact angle of two columns and is responsible for the high growth exponent.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support of the DFG via SFB 345 and stimulating discussions with S. Schneider and G. v. Minnigerode. This work has benefited from the use of IPNS which is funded by U.S. DOE, under contract W-31-109-ENG-38 to the University of Chicago.

REFERENCES

1. Collver, M.M. and R.H. Hammond, Phys. Rev. Lett. **30**, 92 (1973).
2. Bergmann, G., Phys. Rep. **27C**, 161 (1976).
3. Reid, J.S., *et al.* Thin Sol. Films **236**, 319 (1993).
4. Hecht, H., *et al.*, Z. Physik B **100**, 47 (1996).
5. Nicolet, M.-A, Appl. Surface Science **91**, 269 (1995).
6. Barabasi, A.-L., Fractal concepts in surface growth, (Cambridge University Press, 1995).
7. Bicker, M., U.v. Hülsen, and U. Geyer, to be published.
8. Wolf, D.E. and J. Villain, Europhys. Lett. **13**, 389-394 (1990).
9. Sarma, S.D. and P. Tamborenea, Phys. Rev. Lett. **66**, 325-328 (1991).
10. Geyer, U., U.v. Hülsen, and P. Thiyagarajan, J. Appl. Phys. 1996. **in press**.
11. Dina, S., U. Geyer, and G.v. Minnigerode, Ann. Physik **4**, 623 (1995).
12. Hülsen, U.v., *et al.*, Mat. Res. Soc. Symp. Proc. **356**, 143 (1995).
13. Reinker, B., *et al.*, Mat. Res. Soc. Symp. Proc. **355**, 601 (1995).