SELF-ORGANIZED NANOSCALE MULTILAYER GROWTH DURING THE DEPOSITION OF HYPERTHERMAL SPECIES

Hayo Zutz[1], Inga Gerhards[1], Carsten Ronning[1], Hans Hofsäss[1], Michael Seibt[2], Wan-Yu Wu[3] and Jyh-Ming Ting[3]

[1]II. Physikalisches Institut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
[2]IV. Physikalisches Institut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
[3]Department of Materials Science and Engineering, National Cheng Kung University, 1 University Road, Tainan 701, Taiwan, ROC

Abstract. The quasi-simultaneous deposition of low energy-mass-selected C^+ and either Au^+ or Fe^+ ions resulted in the formation of alternately metal-rich and metal-deficient layers in an amorphous carbon matrix with periods in the nm range. The metal-rich layers consist of densely distributed crystalline particles while the metal-deficient layers are amorphous or contain only smaller numbers of crystalline clusters. A similar structure was found in films grown by reactive dc-magnetron sputtering of Cu, Pt, and Ni targets in an Ar/CH_4 plasma. The multilayer formation can be described by an interplay of sputtering, surface segregation, ion induced diffusion, and the stability of small clusters against ion bombardment.

1. INTRODUCTION

The simultaneous deposition of energetic species of two different elements (co-deposition) usually leads to homogeneously mixed films due to the energy of the atoms used for diffusion and rearrangement processes in subsurface and surface regions [1]. If the involved elements are immiscible, a phase separation with precipitates of one element within the other may occur. The size and distribution of such clusters is strongly dependent on the deposition parameters such as ion energy, provided stoichiometry and temperature [2]. A number of studies have shown that this phase separation process can also result in the formation of a self-assembled multilayer structure [3-7]. This structure appears in particular under certain deposition conditions for the co-deposition of carbon and certain metals, including the carbide forming metals Fe and Ni [3,4]. These studies reveal that alter-

nating nanoscale layers of carbon and metal were obtained after co-deposition of the respective energetic species, but with two different methods: mass selected ion beam deposition (MSIBD) and dc-reactive magnetron sputter deposition, respectively.

The model of Gerhards *et al.* presented in ref. [4] explains the formation of a multilayer structure by segregation of the metal atoms to the film surface (fraction f_{surf}). The atoms will form clusters on the surface which will be partially sputtered by impinging carbon and metal ions with a total metal sputtering yield of S_M. These clusters are basically stable against ion bombardment. The carbon ions, which were implanted in these clusters, will segregate to the cluster surface and fill the gap between the clusters. The carbon atoms overgrow the cluster layer and the buried layer ceases to grow if neither carbon nor metal contribute to its growth. This process results in a layered structure of alternat-

Corresponding author: Hayo Zutz, e-mail: hzutz@uni-goettingen.de

ing carbon rich / metal deficient and carbon deficient / metal rich layers. The layer distance is determined by the total metal sputtering coefficient S_M and the fraction of metal atoms segregating to the surface f_{surf}.

In this work, we report on the experimental results of the multilayer formation. The aim was to test the predicted variation of the layer period with the ion energy and the fluence ratio from the model developed in ref. [4]. The second aim was to investigate the multilayer formation for the carbide-forming system a-C:Ni by means of MSIBD. In this case, multilayer formation had been observed when employing dc magnetron sputter deposition. We wanted to test whether Ni behaves like the carbide-forming system a-C:Fe also presented in ref. [4].

2. EXPERIMENTAL

Two different methods for co-deposition of films containing different metals (Au, Fe, Ni) in an amorphous carbon matrix were employed. The first method was reactive dc magnetron sputtering with one single target containing the high-purity metal. The argon/methane gas flow ratio was varied from 1/2 to 15/1 at a total flow of 12 sccm by means of a mass flow controller. The total pressure was set at 1.33 Pa and the discharge power was 100 W. The silicon substrates (p-Si, <100>, ~1 cm², 10 Ω/cm) were grounded and not heated during deposition. Details of the experimental setups are described elsewhere [3,8].

The second method, Mass Selected Ion Beam Deposition (MSIBD), allows to grow films where only the selected ion species with a given kinetic energy contribute to the film growth [9]. In this work, an ion energy of 150 eV was used for the a-C:Au and of 100 eV for the a-C:Ni films. The fluence ratio of carbon ions to metal ions $r_{fluence} = f_C / f_{Me}$ was set to $r_{fluence} = 80/20 = 4$ in the case of a-C:Au and $r_{fluence} = 90/10 = 9$ in the case of a-C:Ni. The a-C:Au film was grown without using the beamsweep, which normally ensures homogeneous deposition over the whole substrate area by scanning the beam over the entire substrate. This results in a locally varying fluence ratio. The Si substrate was kept at room temperature during deposition. Before starting the co-deposition, the p-Si substrate was sputter-cleaned by bombardment with 1 keV $^{40}Ar^+$ ions and then coated with a pure a-C layer of some 10 nm thickness. A more detailed description of the experimental setup and the theoretical treatment of the deposition process can be found in refs. [10-12].
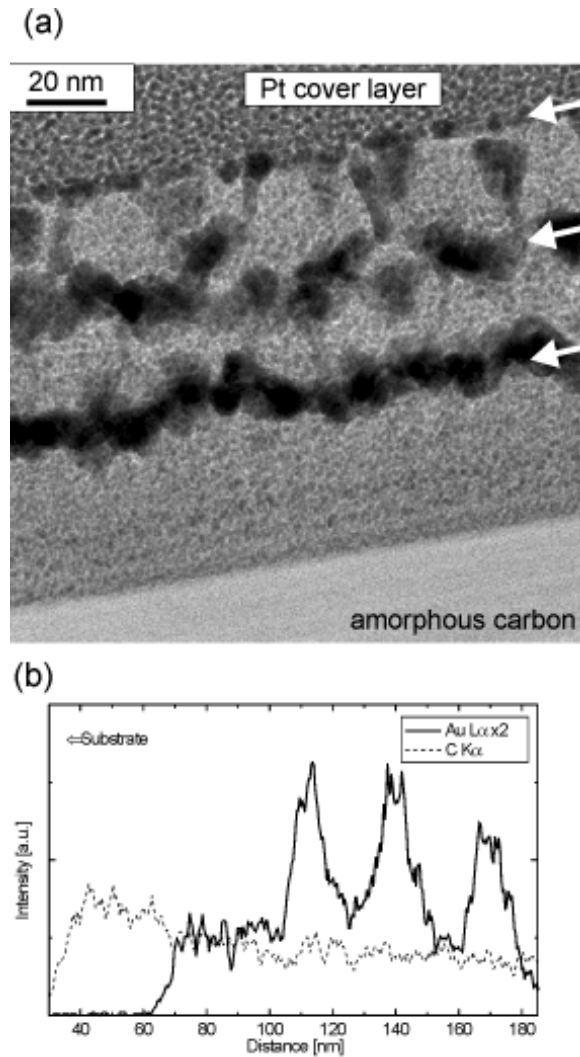

Fig. 1. (a) TEM micrograph in position I of an a-C:Au film prepared by MSIBD using an ion fluence ratio of C/Au = 80/20 and ion energies of ~150 eV at RT on a-C on p-Si. The three well-defined Au-rich layers of ~10 nm thickness (indicated by white arrows) have a layer periodicity of ~30 nm. These layers correspond to the maxima in the Au signal in the EDX-line scan (b). The Pt-cover layer is deposited on the film in the process of TEM preparation using the FIB.

The films were analyzed by Rutherford Backscattering Spectroscopy (RBS) at the Göttingen heavy ion implanter IONAS, using a 900 keV He^{++} beam [13], Transmission Electron Microscopy (TEM), and Energy Dispersive X-ray spectroscopy (EDX) with a Phillips CM200-UT. The cross-sec-

Fig. 3. Rutherford Backscattering Spectroscopy of the a-C:Au film shown in Fig. 1 and Fig. 2. The solid lines are simulations using the RUMP Package [16].
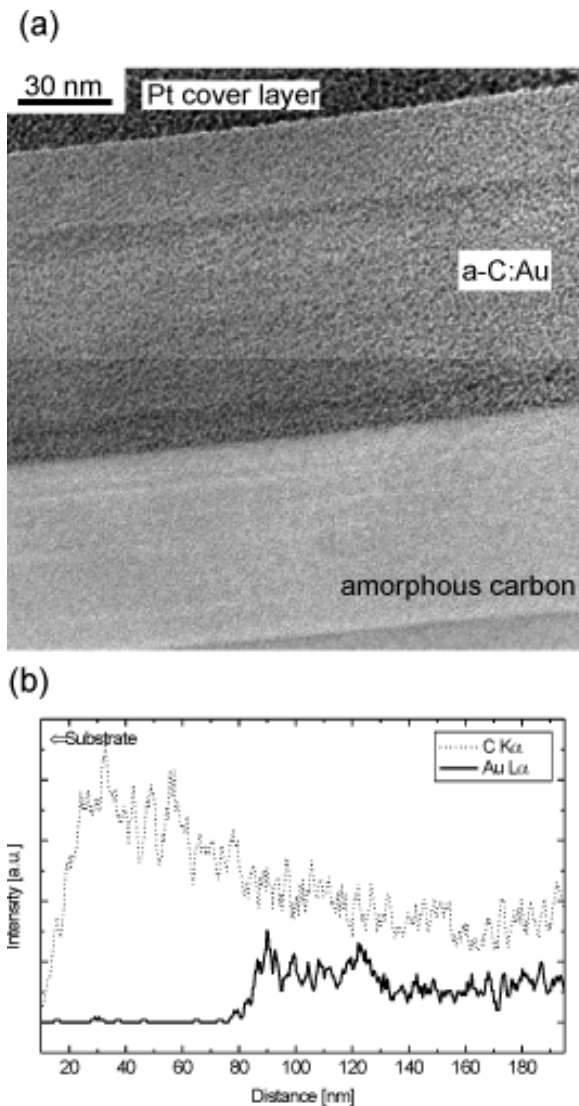

Fig. 2. (a) TEM micrograph of the film shown in Fig. 3 in position II. The Au clusters are homogeneously distributed in the film. (b) The EDX-line scan also reveals a homogeneous distribution of the Au in the film.

tional TEM-samples were either prepared by using a Focused Ion-Beam (FIB) system (FEI Nova 600 Nanolab) or by sandwiching, grinding, polishing and ion milling.

3. EXPERIMENTAL RESULTS

The first experiment was the synthesis of an a-C:Au film deposited by MSIBD. Compared to previous studies carried out at an ion energy of 100
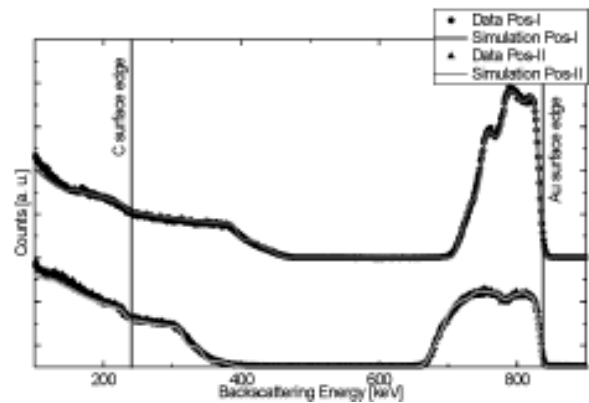
eV [4], this film was deposited at an ion energy of 150 eV. As predicted by the model proposed by Gerhards *et al.* [4], sputtering of Au becomes more severe, compared to a 100 eV deposition, and is expected to result in a larger layer period or a missing layer structure. Two spots of 1 mm² of the a-C:Au film were analyzed with TEM, EDX, and RBS. In the TEM image of spot I (Fig. 1a), three Au-rich layers are clearly visible. The EDX-line scan (Fig. 1b) shows three clearly distinguishable Au-rich and C-deficient layers, separated by Au-deficient and C-rich layers. The maxima in the EDX-line scan correspond to the Au-rich layers indicated by the arrows. The layer periodicity of the ~10 nm thick Au-rich layers is around 30 nm and the Au-rich layer contains densely distributed crystalline Au-clusters with diameters around 8 nm. The Au-deficient layers contain smaller Au-clusters with maximum diameter of 4 nm embedded in an a-C matrix. In the second spot (position II), the TEM image shown in Fig. 2a reveals a homogeneous cluster distribution over the whole film thickness, which is confirmed by the EDX-line scan (Fig. 2b). Fig. 3 shows the RBS spectra of both spots. For position I the three maxima in the Au-signal correspond to the three Au-rich layers visible in the TEM image. For position II, the spectrum reveals an almost homogeneous Au distribution in the film.

In the second experiment, a-C:Ni films were grown by dc-magnetron sputtering using an argon/methane ratio of 3/2 and 5/2 and a substrate tar-
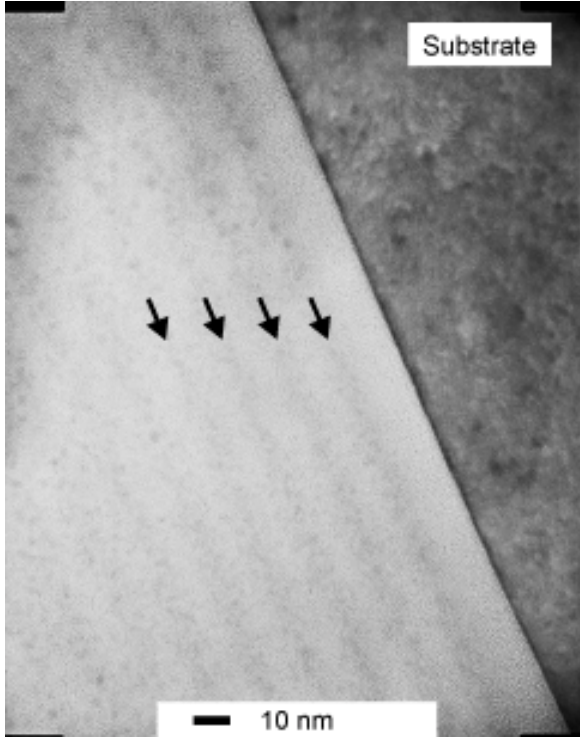
Fig. 4. TEM micrograph of an a-C:Ni film grown with an argon/methane ratio of 3/2 at 1.33 Pa and without applying any heating or bias. Several layers with a layer period around 10 nm can be observed, indicated by the black arrows.

Fig. 5. TEM micrograph of an a-C:Ni film prepared by MSIBD using an ion fluence ratio of C/Ni = 90/10 and ion energies of ~100 eV at RT on a-C on p-Si. The Ni clusters are homogeneously distributed in the film. The Pt-cover layer is deposited on the film in the process of TEM preparation using the FIB.

get distance of 5 cm without any bias or heating of the substrate. The TEM image (Fig. 4) of a sample grown with a gas ratio of 3/2 shows a pronounced layered structure, with a layer period of about 10 nm. A film grown with an argon/methane ratio of 1/2 (i.e. a smaller amount of sputtered metal atoms) does not show any layered structure. An a-C:Ni film grown by MSIBD with 100 eV Ni⁺ and C⁺ ions with $r_{fluence} = 9$, resulting in a total metal sputter coefficient $S_M = 3.4$ (calculated using SRIM [15]), could lead to an internal layer formation like Fe (i.e. $f_{surf} \sim 0$) or instead to a homogenous metal cluster distribution like Au, Cu (i.e. $f_{surf} > 0$, $S_M > 1$) [4]. The film shows homogeneously distributed clusters within the amorphous carbon matrix and no layered structure (Fig. 5). RBS reveals that only 34% of the deposited Ni-ions are actually incorporated in the MSIBD-grown film, resulting in an overall metal sputter loss of ~0.7 due to sputtering of Ni by Ni and C ions.
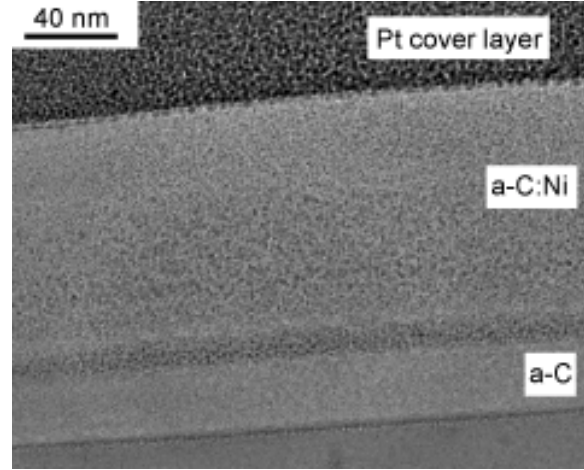
4. DISCUSSION

The a-C:Au film is a test of the model described in ref. [4], based on the segregation of one element to the film surface (in this case: Au) and the stability of small clusters of this element against ion bombardment. For given deposition parameters and a given layer thickness d_M of the Au-rich layer extracted from the TEM images, it is possible to calculate the layer period t using equation 5 of ref. [4]:

$$t = d_M \left[1 + \frac{n_M c}{(1 - S_M) f_{surf}} \times \left(\frac{1}{n_c} r_{fluence} (1 - s_{cc}) + \frac{1}{n_M} (1 - f_{surf}) \right) \right].$$

There are two parameters which depend on the ion energy and the fluence ratio $r_{fluence}$: The total metal sputtering coefficient $S_M = r_{fluence} \cdot S_{CM} + S_{MM}$ (where S_{CM} is the sputtering of metal atoms by impinging carbon ions and S_{MM} is the sputtering of metal atoms by impinging metal ions) and the fraction of Au-atoms segregating to the surface. S_M can be calculated by SRIM and increases with increasing ion energy and fluence ratio. If S_M increases the layer period t should also increase.

Table 1.

System	Fluence ratio $r_{fluence}$	Deposition energy [eV]	Layer period t [nm]	
a-C:Au	4	100	12	[4]
a-C:Au	1.9	150	30	this work
a-C:Au	4…7	150	8	this work
a-C:Ni	9	100	8	this work

Due to the deposition process in this specific case, the local fluence ratio $r_{fluence}$ is unknown, but it can be determined using the information from the TEM images and the RBS spectra (atomic densities: $n_M = 59$ nm^{-3}, $n_C = 110$ nm^{-3}). The thickness of the Au-rich layer in spot I is $d_M \approx 10$ nm, the layer periodicity is $t \approx 30$ nm and the coverage fraction of one Au-rich layer is $c \approx 0.4$. Using SRIM [15] sputter coefficients of the impinging C-ions on the deposited C-atoms ($S_{CC}=0.11$), we calculate the deposited number of C-ions to be: $\Phi_{C,dep} \approx 1 \cdot 10^{18}$ cm^{-2}. With the equation above, the number of deposited Au-ions is calculated to be: $\Phi_{Au,dep} \approx 5 \cdot 10^{17}$ cm^{-2}. This leads to a fluence ratio of $r_{fluence} \approx 2$ and a fraction of Au-atoms segregating to the surface of $f_{surf} \approx 0.86$. With this result, the total metal sputtering coefficient can be calculated to be $S_M \tilde{} 0.8$. Thus compared to a 100 eV deposition, S_M increases from ≈ 0.5 to ≈ 0.8, but still remains <1, which explains the larger layer period obtained at an ion energy of 150 eV (see Table 1).

For the second spot (position II) the RBS and TEM data yield: $\Phi_{C,dep} \approx 2 \cdot 10^{18}$ cm^{-2}. This leads to an estimated fluence ratio of $r_{fluence} \approx 4…7$ and a fraction of Au-atoms segregating to the surface of $f_{surf} \approx 0.7…0.8$. In this case, $S_M \approx 1.4…1.5 >> 1$ so that no layers can be formed due to severe sputtering of Au and the value for f_{surf} is somewhat smaller than in position I due to the missing Au deposition into the Au-clusters on the surface. The results are summarized in Table 1.

The second set of samples shows that it is possible to grow multilayer a-C:Ni films using reactive magnetron sputter deposition by carefully choosing the deposition parameters. For MSIBD grown films the sputtering loss of 0.7 determined from the RBS data for the MSIBD-grown film reveals that - like Au and Cu - Ni partially segregates to the film surface. Due to the overall metal sputter coefficient of $S_M \approx 3.4$ calculated by SRIM [15], all Ni-atoms on the surface will be sputtered off. Knowing this, the fraction of Ni segregating to the surface can estimate to be: $f_{surf} \approx 0.7$. Ni behaves obviously differently from the carbide-forming metal Fe, which does not segregate to the surface at all and is therefore not exposed to sputtering and shows layer formation [4]. A layered a-C:Ni film structure requires a reduction of $r_{fluence}$ to values $r_{fluence} < 2$ for 100 eV C$^+$ and Ni$^+$.

5. CONCLUSIONS

Self-organized alternating carbon and metal layers have been prepared by co-deposition of energetic carbon and metal atoms using reactive magnetron sputter deposition and MSIBD. The new results confirm the model presented in ref. [4]. In agreement with the predictions of the model [4], the layer distance is increasing with the ion energy (see Table 1). The formation of multilayers in films containing the carbide-forming metal Ni using magnetron sputter deposition was observed. The MSIBD results show that Ni segregates partially to the surface with a fraction of $f_{surf} \approx 0.7$. The multilayer formation in a-C:Ni is expected to occur at a deposition energy of 100 eV deposition with a fluence ratio of $r_{fluence} < 2$.

ACKNOWLEDGEMENT

REFERENCES

[1] H. Hofsäss and C. Ronning, In: *Beam Processing of Advanced Materials*, ed. by

J. Singh, S.M. Copley and J. Mazumder (Conference Proceedings of ASM, 1996), p. 29.

[2] I. Gerhards, C. Ronning, H. Hofsäss, M. Seibt and H. Gibhardt // *J. of Appl. Phys.* **93** (2003) 1203.

[3] W.Y. Wu and J.M. Ting // *Chem. Phys. Lett.* **388** (2004) 312.

[4] I. Gerhards, H. Stillrich, C. Ronning, H. Hofsäss and M. Seibt // *Phys. Rev. B.* **70** (2004) 245418.

[5] C. Corbella, B. Echebarria, L. Ramírez-Piscina, E. Pascual, J. L. Andújar and E. Bertran // *Appl. Phys. Lett.* **87** (2005) 213117.

[6] J. H. He, C. A. Carsosella, G. K. Hubler, S. B. Qadri and J. A. Sprague // *Phys. Rev. Lett.* **96** (2006) 056105.

[7] G. B. Thorwarth, *PhD thesis, Herstellung und Eigenschaften amorpher Kohlenstoffschichten in der Plasma-Immersions-Ionenimplantation* (Universität Augsburg, 2005).

[8] W.Y. Wu and J.M. Ting // *Thin Solid Films* **420-421** (2002) 166.

[9] H. Hofsäss, H. Binder, T. Klumpp and E. Recknagel // *Diamond Relat. Mater.* **3** (1994) 137.

[10] C. Ronning // *Appl. Phys. A* **77** (2003) 39.

[11] C. Ronning, D. Schwen, S. Eyhusen, U. Vetter and H. Hofsäss // *Surf. Coat. Technol.* **158-159** (2002) 382.

[12] H. Hofsäss, H. Feldermann, R. Merk, M. Sebastian and C. Ronning // *Appl. Phys. A* **66** (1998) 153.

[13] M. Uhrmacher, K. Pampus, F.J. Bergmeister, D. Purschke and K.P. Lieb // *Nuc. Instr. and Meth. B* **9** (1985) 234.

[14] D. Babonneau, I.R.Videnovic, M.G.Garnier and P. Oelhafen // *Phys. Rev. B* **63** (2001) 195401.

[15] J.F. Ziegler, J.P. Biersack and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 2003).

[16] L.R. Doolittle // *Nuc. Instr. and Meth. B* **15** (1986) 227.