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Surface and Coatings Technology 163–164 (2003) 300–305

SURFACE & COATINGS TECHNOLOGY

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Pulsed laser deposition: a new technique for deposition of amorphous SiO_x thin films

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Abstract

Pulsed laser deposition (PLD) is a physical vapour deposition coating technique for the production of thin films with complex chemical compositions. One of the main advantages of PLD is that excellent coating properties can be achieved even at low deposition temperatures. However, particulate defects in the growing films resulting from the evaporation process are often mentioned as the most important disadvantages of the PLD process. Unfavourable optical, thermo-physical and mechanical properties of the target material evaporated by laser radiation promote the formation of particulate defects. This paper presents some results on silicon-based PLD-films with reduced density of particulates. Silicon, SiO_x and SiO_2 thin films were deposited by laser ablation from silicon targets with a high power pulsed Nd:YAG laser of 1064 nm wavelength in argon and oxygen containing atmospheres. The substrates were arranged in shaded off-axis geometry. The chemical composition and structure of the films were investigated employing transmission electron microscopy (TEM), secondary ion mass spectroscopy, X-ray photoelectron spectroscopy and ellipsometry. The results demonstrate the capability of PLD for the deposition of SiO_x films with varying composition ($0 \leqslant x \leqslant 2$) by shaded off-axis PLD. The results of TEM and spectroscopic ellipsometry are indicating amorphous film structures in all cases.
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Keywords: Pulsed laser deposition; Laser ablation; Si; SiO_x; Shaded off-axis; Droplet reduction; Physical vapour deposition; Thin film technology

1. Introduction

Pulsed laser deposition (PLD) is a thin film deposition technique which has been successfully applied to an extremely wide range of materials [1]. This technique is based on the interaction of a high power density laser beam with a solid target and presents several unique advantages over other conventional physical vapour deposition techniques, especially when using pulsed lasers. For most compounds, PLD under vacuum or inert process gases results in film compositions close to the target. Modification of the composition of the deposit or synthesis of new compounds can be achieved by working in reactive atmosphere [1].

The PLD of semiconductor and insulator thin films like silicon and silicon oxide has been reported by numerous authors since the early 1970s, e.g. [2–15]. However, there was a serious drawback in producing high quality silicon thin films for semiconducting devices and solar cell applications: the emission of microscopic particulates (e.g. droplets) between 0.1 and 10 μm in size from solid targets during the ablation process. This phenomenon depends on many factors such as roughening of the target surface during the ablation process [4], the fluence and wavelength of the laser [2,4,10,12], the density of the target [1] and the

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PII: S0257-8972(02)00612-6

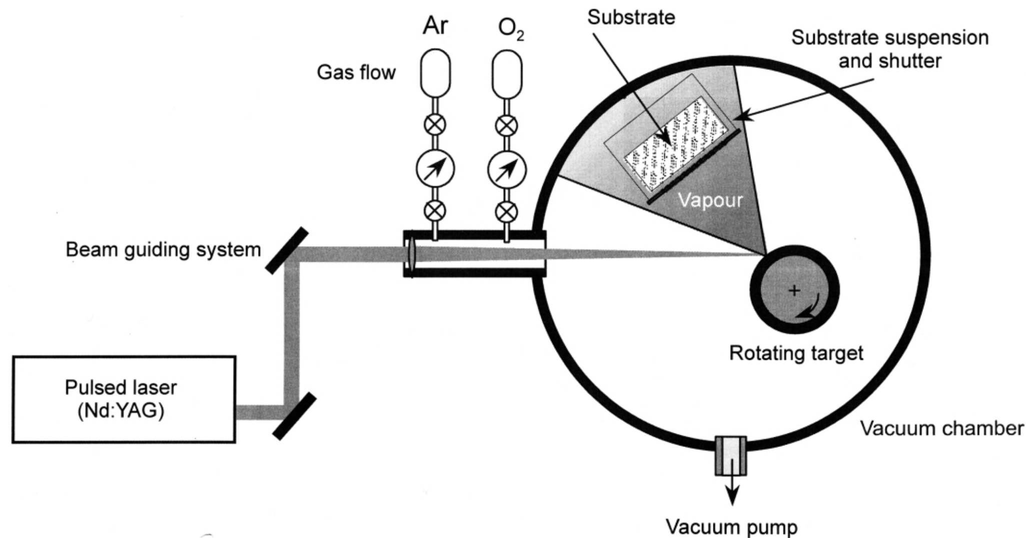

Fig. 1. Schematic view of the PLD system for thin film deposition.

chemical and physical properties of the target material [1]. Agostinelli et al. [16] have shown a number of different solutions for minimizing droplet deposition based on these factors. One approach is the modification of the deposition conditions using the off-axis geometry [17]. In this technique, the substrate is placed perpendicular to the target surface and a low-pressure gas is introduced to scatter the atoms ejected from the target toward the substrate. The heavy particles move straight and only a small fraction of them can hit the substrate. Furthermore, by placing a metallic screen between target and the off-axis mounted substrate nearly all droplets can be screened off from the substrate ('shaded off-axis' geometry) [16]. The aim of this paper is to summarize results of morphological, structural, chemical and optical investigations on high quality SiO_x coatings using the PLD technique in different arrangements.

2. Experimental

2.1. Film deposition

High purity silicon targets (99.95% Si) were used for the ablation experiments using a pulsed Nd:YAG laser, which provides a beam with 1064 nm wavelength, 1 J pulse energy and 10 ns pulse duration at a repetition rate of 10 Hz [18]. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (≈25 °C) onto single crystalline (1 0 0) orientated silicon substrates mounted normal to the target behind a shutter of 1 cm height, see Fig. 1. On the basis of ellipsometric measurements, a uniform native SiO_2 film with a thickness of 2 ± 0.2 nm was present on the in pure acetone resp. pure ethanol ultrasonically cleaned substrates prior to film deposition. The reaction chamber was evacuated before starting the deposition process to pressures below 2×10^{-3} Pa by a pumping unit consisting of an oil diffusion and a rotating pump. During deposition the flows of the process gases (Ar; O_2; mixture of 90 vol.% Ar+10 vol.% O_2) were adjusted by means of electronic mass flow controllers.

2.2. Film characterization

The surface quality of the coatings was inspected with light microscopes. The film structures were examined by transmission electron microscopy (TEM) of cross-sections of films with a thickness of approximately 50 nm using a Philips CM20(LaB_6) transmission electron microscope operating at 200 kV and equipped with a post column imaging filter from Gatan (GIF). For TEM, the preparation included standard procedures like cutting, slicing, polishing and finally Ar^+ ion milling to reach an end-thickness of approximately 50 nm [19].

The characterisation of the chemical film composition occurred by secondary ion mass spectroscopy (SIMS) using a CAMECA IMS 3f [20]. For all measurements, a Cs^+ primary ion beam (primary energy: 6.5 kV, primary ion current: 10 nA) was applied for sputtering the film. $CsSi^+$ and CsO^+ secondary ions from a circular area of approximately 60 μm in diameter were accepted. In order to achieve a homogenous illumination of the sample, the primary beam scanned rapidly over the sample surface, the illuminated area was approximately 250×250 μm^2. The instrument has approximately 2 μm lateral and approximately 20 nm vertical resolution. A thermally oxidized nearly stoichiometric SiO_2 was taken as a standard for quantitative analysis.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical bonding in the films using an Omicron Multiprobe system with a

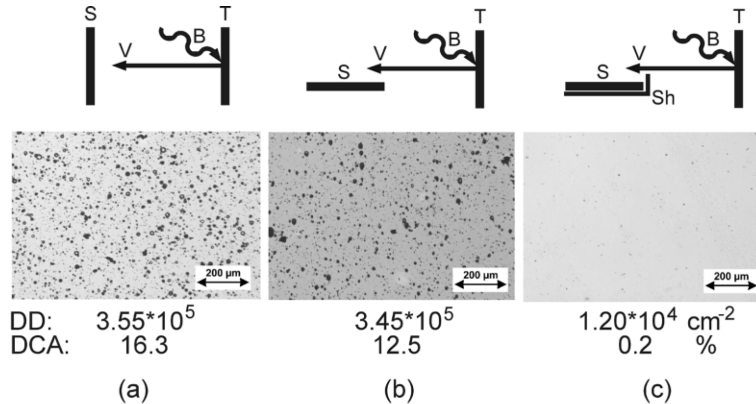

Fig. 2. Schematic diagram of deposition arrangements and top-view micrographs of films deposited in (a) on-axis; (b) off-axis and (c) shaded off-axis geometry (S—substrate, T—target, Sh—shutter, B—incident laser beam, V—ablated metal vapour, DD—droplet density, DCA—percentage of substrate area covered with droplets).

monochromized AlKα (1486.6 eV) X-ray beam and an EA 125 energy analyser [21]. The resolution of this set-up is better than 0.3 eV, and the analysis took place at a pressure of 4×10^{-9} Pa. The spectrometer was operated in the fixed analyzer transmission mode. All binding energies reported in this work were referenced to the binding energy of the carbon C 1s peak at 285.0 eV. The detection sensitivity was approximately 1 mass%. For sputtering a Omicron 'ISE 10' sputter gun using Ar^+ ions was used.

The optical properties of the films were determined using a variable angle spectroscopic ellipsometer (J.W. Woollam Comp. Inc.) at angles of incidence between 65 and 85° in the spectral range from 240 to 1100 nm with 2 nm spectral resolution.

3. Results and discussion

3.1. Film deposition

To optimise film quality, silicon coatings were deposited in various experimental set-ups (on-axis; off-axis; shaded off-axis geometry) by varying the target—substrate distance, the process gas pressure and the type of gases. Fig. 2 shows the film surface in the three geometrical arrangements. It indicates no pronounced differences in the droplet density ($\sim3.5\times10^5$ cm^{-2}) and the droplet covered area (approximately 14% of the whole surface) for films deposited in on-axes and off-axis geometry. In contrast the shaded off-axis geometry turns out a significant reduction of the particle density to approximately 1.2×10^4 cm^{-2} and the droplet covered area to approximately 0.2% as average values of all examined films. The average droplet size is approximately 20 times smaller in shaded off-axis geometry deposited coatings. On silicon films only spherical droplets can be detected whereas most particulates found on reactively deposited films (O_2 and Ar/O_2 as process gas) have spattered shape. This is caused by brittle SiO_2 layers on the target during laser ablation which burst during laser irradiation [1].

For studying the scattering of atoms and ions on their way from the target to the substrate the gas pressure was varied during deposition. The highest deposition rate was found for a pressure of approximately 0.8 Pa. The results obtained indicate that there is no influence of the process gas pressure on the droplet density in case of the shaded off-axis set up.

The film thicknesses, determined by spectroscopic ellipsometry, and the film deposition rates are shown in Table 1. The significant higher deposition rates of samples S2, S3 and S4 are due to the incorporation of oxygen atoms resulting in SiO_x films. The deposition rates found in the experiments are in the same order of magnitude than those reported in Refs. [2,4,10,13]. Furthermore, a good uniformity of the film thicknesses on the 1×1 cm^2 large silicon wafers was found.

3.2. Film structure

Fig. 3 shows TEM results of a film deposited in pure Ar atmosphere (film S1) and a film deposited in an Ar/O_2 atmosphere (film S4). No indications of a crystalline structure could be found in the TEM investigations which is in contrast to published data for SiO_2 and silicon films [8,15]. The amorphous structure of the films is also indicated by ellipsometric measurements (Section 3.4). The reasons for the growth of amorphous SiO_x films in the shaded off-axis placed substrates area probably the lower kinetic energy of the deposited species after collisions with process gas atoms as well as the low deposition temperature (≈25 °C), resulting in less activation of surface diffusion.

3.3. Chemical composition of the films

In order to get quantitative information about the chemical composition, SIMS and XPS investigations

Table 1
Process gas fluxes, oxygen partial pressures, film thicknesses and deposition rates of SiO_x films deposited in shaded off-axis geometry

Sample	Ar (sccm)	O_2 (sccm)	Gas mixture 10% O_2 +90% Ar (sccm)	Calculated O_2 partial pressure (Pa)	Film thickness (nm)	Deposition rate (nm/pulse)
S1	30	0	0	<0.001	84	2.3×10^{-3}
S2	15	0	15	0.05	128	3.5×10^{-3}
S3	25	5	0	0.14	130	3.7×10^{-3}
S4	15	15	0	0.37	117	3.3×10^{-3}

were performed. Table 2 shows the results of SIMS measurements of the films produced in different gas atmospheres. Fig. 4 shows the depth profiles of the oxygen concentration in at.%. Compared to ellipsometry results the film thicknesses measured by SIMS are slightly lower because of differing sputter rates of the SiO_2 standard and the SiO_x films. The results indicate that understoichiometric SiO_x films can only be deposited in atmospheres of very low oxygen partial pressure, e.g. mixtures of 95% Ar and 5% O_2. The oxygen content in film S1 indicates a nearly pure silicon film with an oxygen peak in a depth of approximately 64 nm as a remnant of the natural oxygen containing film on the silicon wafer substrate. The decreasing oxygen content from this depth towards the surface of the film results from remaining oxygen containing gas in the deposition chamber at the beginning of the process. All other films show no significant variations of the Si/O ratio across the coatings thickness.

Additional XPS investigations were carried out in various depths in order to study the nature of chemical bonding within the films. Fig. 5a shows a comparison of the silicon peaks obtained for film S1 at the surface and at depths of 20, 40, 60 and 80 nm. At the surface, besides the Si 2p1/2 Peak at 99.3 eV corresponding to Si^0, a second peak is present at 103.0 eV which can be related to Si^{4+}. This peak vanishes with increasing depth indicating that the film surface is covered with a layer of natural SiO_2 with a thickness of approximately 5 nm caused by handling of the coated samples in air. At 60 nm, which is near the surface of the original silicon wafer, a mixture of different oxidation states of silicon was found. This is in accordance with the SIMS investigations (Fig. 4) which reveal an oxygen peak at the film/silicon wafer interface. Fig. 5b shows the XPS spectra of film S1 in a wider energy range indicating the presence of silicon (99.3 and 103.0 eV), oxygen (532.5 eV), carbon (285.0 eV) and argon (242.0 and 243.9 eV). While the first two elements are used to form the film, contamination of so called ambious carbon is due to probe handling or storage in air or from the vacuum system. Both, oxygen and carbon peaks decrease with increasing depth, strongly reappearing at the film/silicon wafer interface at 60 nm. In addition, the oxygen peak appears at 531.5 eV indicating that oxygen is physisorbed between the laser pulses

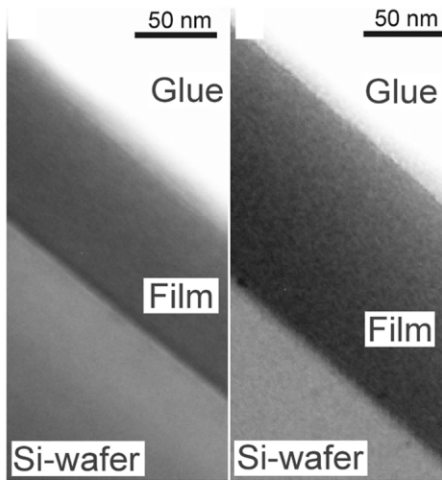

Fig. 3. Bright field TEM images of cross-sections of film (a) S1 and (b) S4.

Table 2
Average atomic oxygen concentration and calculated stoichiometry of SiO_x films determined by SIMS

Sample	O (at.%)	Stoichiometry
S1	0.8	$SiO_{0.008}$
S2	48.9	$SiO_{0.96}$
S3	64.6	$SiO_{1.83}$
S4	66.2	$SiO_{1.96}$

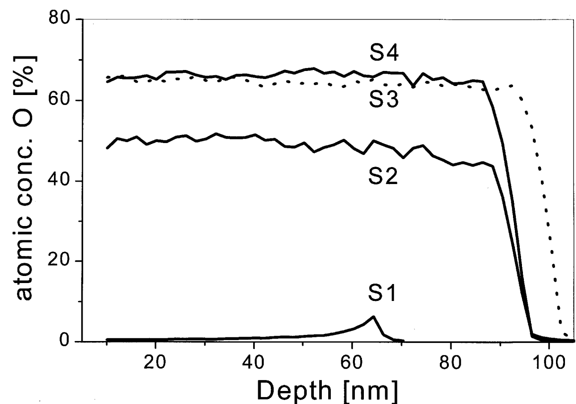

Fig. 4. Depth profile of the oxygen atomic concentration investigated by SIMS.

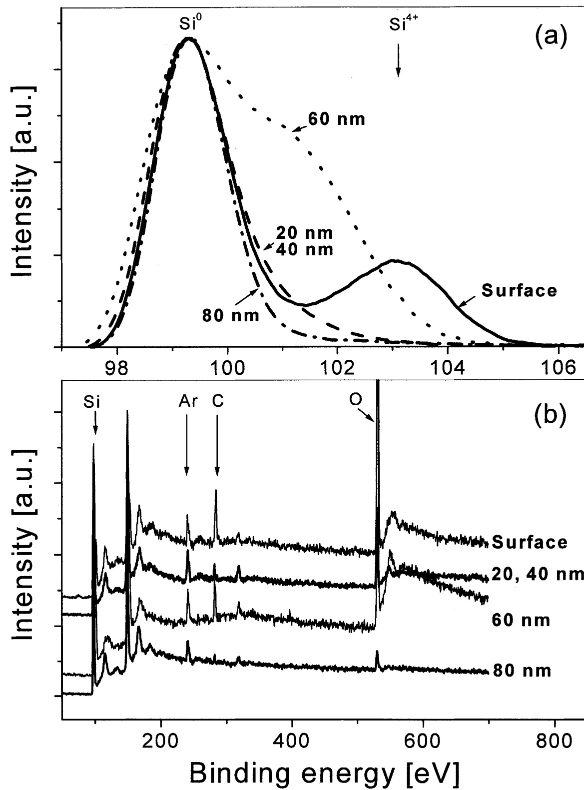

Fig. 5. XPS spectra taken from the surface and at depths of 20, 40, 60 and 80 nm below the original surface (a) energy range from 50 to 850 eV to show the silicon excitation states; (b) energy range from 97 to 106.5 eV to show further elements (spectra normalized to the Si^0 peak at 99.3 eV).

from the process atmosphere in form O_2 molecules and later in the deposition process covered with Si atoms again. This result is confirmed by the measurement of the silicon peak, which reveals that no Si^{4+} is found in the film. Argon, on the other hand, is present because it is used as process gas during the PLD process. Implantation effects from the sputtering process are unlikely because argon is already present at the surface prior argon sputtering.

A comparison of the XPS spectra of all films at a depth of approximately 40 nm is shown in Fig. 6. Silicon (99.3 and 103.0 eV), oxygen (532.5 eV) and argon (242.0 and 243.9 eV) were found in all four films. While in film S1 silicon can be found at 99.5 eV corresponding to Si^0, it appears at a binding energy of 103.0 eV in the other films, which can be attributed to Si^{4+}. In accordance with that, a high amount of oxygen appears at a binding energy of 532.5 eV corresponding to O^{2-}, indicating SiO_2 type bonding. In the silicon film (S1), less oxygen is present at 531.5 eV which can be attributed to O 1s (O_2). Thus, while oxygen is present due to the SiO_2 formation in the coatings which were produced in argon/oxygen atmosphere, a small amount of oxygen in form of O_2 impurities is present

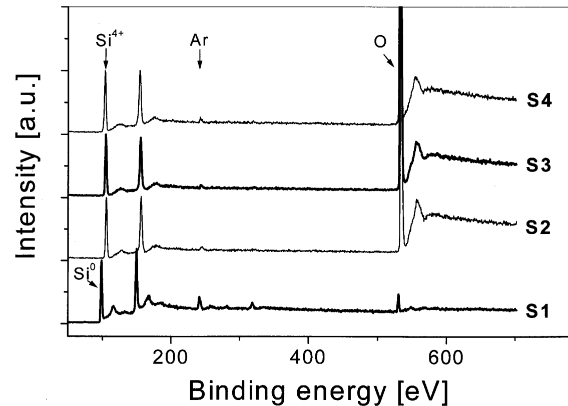

Fig. 6. XPS spectra of the films S1, S2, S3 and S4 taken at a depth of 40 nm below the original surface (spectra normalized to the silicon peak at 99.3 and 103 eV, respectively).

in film S1, deposited in pure Ar atmosphere. A small amount of argon is present in all films in an amount of some weight percent, which decreases with decreasing Ar gas flow during film deposition.

3.4. Measurements of optical constants

Optical constants were investigated by spectroscopic ellipsometry at wavelengths between 240 and 1100 nm. To fit the measured data and get quantitative information about the index of refraction n and the absorption coefficient k the Cauchy dispersion [23] and the Urbach relation [24] were applied, respectively. In all cases fitting with data of amorphous silicon [22] (for sample S1) or amorphous SiO_2 [22] (for samples S2, S3 and S4) brought the best approximations, indicating amorphous film structures in accordance with TEM investigations. Fig. 7 shows the ellipsometric data for the silicon film S1 and Fig. 8 for the silicon oxide films S2, S3 and S4: The results indicate very good accordance of n and k with data for amorphous films [22]

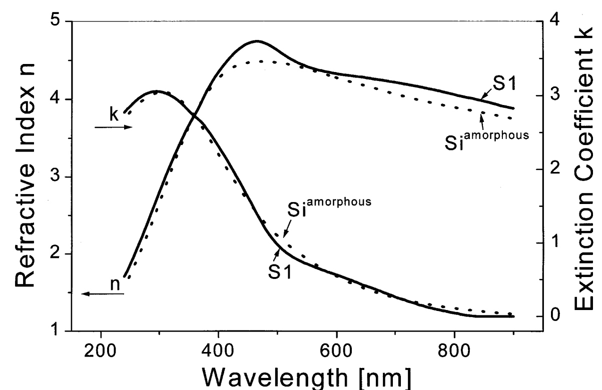

Fig. 7. Spectral variations of refractive index n and absorption coefficient k of nearly oxygen free silicon films compared with data of amorphous silicon ($Si^{amorphous}$) [22].

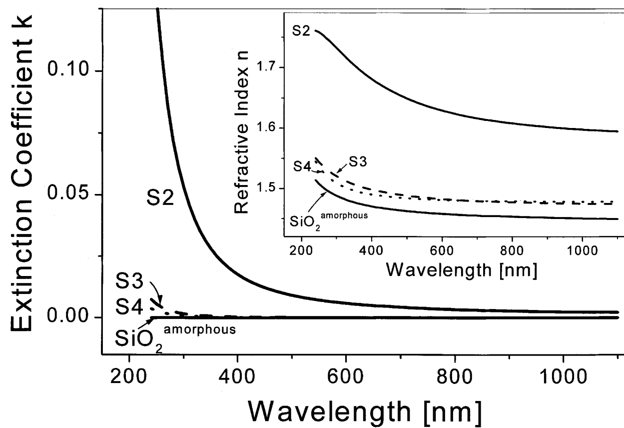

Fig. 8. Spectral variations of absorption coefficients k and refractive indices n of oxygen containing SiO_x films (S2, S3, S4) compared with data of amorphous SiO_2 ($SiO_2^{amorphous}$) [22].

especially for the film S1. Films S3 and S4 show slightly higher values because of deviation from stoichiometry. Much higher n and k values were observed for film S2, probably caused by the significantly lower oxygen content compared to the stoichiometric composition.

4. Conclusions

Nearly droplet free silicon and SiO_x thin films were deposited on shaded off-axis placed silicon wafers by pulsed laser ablation of silicon targets at deposition rates of approximately 2×10^{-3} to 4×10^{-3} nm/pulse. SIMS and XPS investigations reveal the strong effect of the oxygen partial pressure during deposition on the composition of SiO_x films. Sub-stoichiometric films can only be achieved in atmospheres with a low oxygen partial pressure. The XPS investigations indicate further that oxygen is present in silicon oxide films in SiO_2 type bonding, whereas silicon films contain oxygen in O_2 type bonding. All films show an amorphous structure, which is probably caused by the low kinetic energy of deposited atoms and ions in the shaded off-axis technique. The optical properties of nearly stoichiometric silicon and SiO_2 thin films are in good accordance with thermally grown amorphous films.

Acknowledgments

Financial support of this work by the Austrian Federal Ministry of Traffic, Innovation and Technology, the Government of Styria, the Technologie Impulse Gesellschaft mbH in the frame of the Kplus Programme and the European Union is highly acknowledged. The authors are grateful to Prof. F. Hofer (Zentrum für Elektronenmikroskopie, Graz) for the TEM investigations and to DI J. Hagler and DI M. Fleischanderl (voestalpine Stahl GMBH, Linz) for their assistance and valuable discussions.

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