Tuning the microstructure of the Pt layers grown on Al₂O₃ (0001) by different sputtering methods

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ABSTRACT

High-quality epitaxial Pt films are usually grown by molecular beam evaporation (MBE) techniques, where the deposited atoms reach the substrate with typical thermal energies. To obtain a good epitaxial growth, the substrate is kept at elevated temperatures ranging between few hundred to thousand degrees. While the epitaxial quality improves at higher substrate temperatures, above a critical temperature Volmer-Weber growth mode starts and causes a rough film morphology. Here, we use a new type of facing target cathode (FTC) to grow Pt onto Al₂O₃ (0001) substrates. In contrast to conventional sputtering sources, FTC sources provide adatoms with lower kinetic energies, but higher growth rates compared to MBE. In this study, the crystal structure of Pt films is compared for different substrate temperatures. Using FTC, flat Pt films with low strain and a morphology that is either nanocrystalline or highly epitaxial could be grown through proper choice of substrate temperature.

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Noble metal thin films have diverse applications, ranging from corrosion resistant electrodes, seed layers to design the crystalline structure of the subsequent metallic [1] or non-metallic films, [2] and catalysis [3]. Pt layers, in particular, are used in many different applications due to their low resistivity, thermal and chemical stability and crystal structure [4–6]. Often, Pt is used as a seed- and/or barrier layer, wherein its high density, low reactivity and crystal texture are convenient. For example, epitaxial cubic Pt layers can support the growth of lead zirconate titanate (PZT) layers and can be utilized as the electrode layers for micro electro-mechanical system (MEMS) applications [7,8]. The epitaxial growth of cubic Pt requires specific deposition conditions for different substrates. Better epitaxy of Pt films is usually achieved at high temperatures, which increases the mobility of the growing atoms on the film/substrate surface. However, above a certain critical temperature, further increase in mobility of the deposited atoms can lead to a Volmer-Weber type growth resulting in islands and deeper trenches between these islands. Accordingly, this leads

to a very rough film morphology causing an increase in the sheet resistance [9,10]. Such an unwanted trench formation could be prevented at least partially either by increasing the thickness of the Pt layer [10] or by incorporating different gases such as oxygen during the growth [11]. Trivially, increasing the Pt layer thickness requires longer deposition times and more material consumption, making it inefficient. Also, Pt is commonly used in flexible electronics as an electrode layer. Flexible devices require materials with smaller grains in order to handle high mechanical strains without forming cracks [12]. Accordingly, an ideal deposition method to cover different applications should allow the adjustment of the adatom energies over a range including typical thermal energies to several electron volts as obtained for conventional sputter-deposition sources, provide a high deposition rate and permit the deposition of different materials including materials with high melting points and low vapor pressures at moderate operating temperatures.

In this study, we employ both conventional and facing target cathode (FTC) sputter sources to deposit thin Pt films onto Al₂O₃ (0001) single crystalline substrates kept at temperatures ranging from room temperature to 400 °C. Note that the maximum temperature is limited by the specific experimental setup used here. The FTC sputtering source used for this study was designed and

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Fig. 1. 2 theta-theta scans of Pt films grown by conventional magnetron sputtering (a) and FTC sputtering (b). All scans are normalized to the Al₂O₃ (0006) peak intensity. Lower panels show the omega scans (rocking curve) of Pt films grown by conventional sputtering (c) and FTC sputtering (d). Data in (c) and (d) are shifted vertically for better visibility.

fabricated by Evatec AG. The FTC source consists of two targets facing each other and the magnetic field is confined between the targets. The substrate is placed perpendicular to the targets surfaces to obtain an off-axis deposition geometry. The deposition pressure was set to 1.7 microbar of Ar and high purity Pt targets (99.999%) were used. The deposition parameters such as power, distance, etc. were kept the same for all samples of a given deposition type. It is also worth noting that DC deposition power for conventional sputtering setup was set to the lowest power (20 W) at which a stable plasma could be sustained. The deposition rates were calibrated using X-ray reflectometry measurements performed on Pt films deposited onto oxidized silicon wafers at room temperature. These rates were then used to grow all films to a nominal thickness of 13 nm. Crystalline structure of the films were investigated by means of X-ray diffraction (XRD) methods. The symmetric 2 theta-theta scans and rocking curves (RCs) were recorded on a standard Bruker D8 Discover with DaVinci Design equipped with a Cu-K α radiation source. Reciprocal space maps (RSM) and pole figures were obtained by using a Bruker D8 Advanced DaVinci diffractometer equipped with a Cu K α radiation source together with high-resolution optics to limit the angular and energetic dispersion of the primary beam. Atomic force microscope (AFM) images were taken with a Bruker Dimension Icon microscope setup under ambient conditions.

Fig. 1 a and b display the 2 theta-theta scans acquired from the nominally 13 nm-thick Pt films deposited at RT, 100 °C, 200 °C, 300 °C and 400 °C substrate temperatures by conventional magnetron and FTC sputtering, respectively. All of the data are normalized to the (0006) Al₂O₃ substrate peak intensity. All samples show

only Pt (111) peak (apart from the substrate peak) and hence a (111) texture. In 2 theta-theta scans, the peak height and width are proxies for the crystalline quality of the Pt film, while the peak position reflects the strain-induced distortion of the lattice along the orientation direction. For the film grown by conventional sputtering at room temperature, a well-defined Pt (111) peak is observed. At higher temperatures, the Pt (111) peak becomes more intense as the substrate temperature increases from room temperature to 200 °C. Above 200 °C, a further increase of the substrate temperature however leads to lower Pt (111) peak intensities and thus to a degradation of the crystalline quality of the Pt films. Such a degradation of the crystalline quality with increasing temperature has also been observed previously for Pt films grown by molecular beam epitaxy, albeit at higher temperatures, i.e. above 650 °C [5]. In contrast to the films deposited by conventional sputtering, the films grown by FTC show a monotonic increase of the Pt (111) peak intensity with increasing substrate temperature (between RT and 400 °C). The film deposited at RT by FTC shows a very low normalized peak intensity below 0.1, whereas the film deposited by conventional sputtering shows a normalized intensity above 0.2. On the other hand, the peak intensity of the FTC-deposited film at 400 °C substrate temperature is the highest of all films discussed here indicating the best film quality.

In a 2 theta scan, the peak width is governed by the dimension of the crystallites in the vertical direction, that is limited by the film thickness for epitaxial films and 13 nm thickness is aimed for all films grown here. The film thickness can be estimated from the Laue oscillations for epitaxial films. The film thickness of around (13 ± 2) nm was obtained by fitting the Laue fringes for all films

Table 1

2 theta Bragg position and out-of-plane strain values obtained from Pt (111) peaks by performing 2 theta-theta scans and full-width at half-maximum (FWHM) values obtained from rocking curve measurements. T represents the substrate temperature for the samples grown by conventional (conv.) magnetron and facing target cathode (FTC) sputtering.

T	Pt (111) pos. (°) ($\pm 0.01^\circ$)		strain (%) ($\pm 0.03\%$)		RC FWHM (°) ($\pm 0.01^\circ$)	
	conv.	FTC	conv.	FTC	conv.	FTC
RT	39.42	39.78	0.81	0.08	0.69	4.13
100	39.58	39.80	0.43	0.13	0.49	3.30
200	39.74	39.78	0.03	0.07	0.44	0.41
300	39.44	39.80	0.78	0.12	0.53	0.40
400	39.40	39.80	0.86	0.12	0.73	0.33

studied here with the exception of the film grown by conventional sputtering at 400 °C substrate temperature. This is due to the fact that Laue oscillations are sensitive to crystalline disorder and thus provide information on the size of the ordered volume. Therefore, lower thickness values can be obtained from Laue fringes of disordered films, if the ordered volume is smaller than the thickness.

The shift of the peak positions in 2 theta scans that are observed for the films deposited by conventional sputtering (Fig. 1a) arise from the changes of the d_{111} spacing. For example, shift towards smaller 2 theta angles results in swelling of the d_{111} spacing and can be attributed to the presence of an in-plane compressive stress [13]. Interestingly, the compressive stress of the films grown by conventional sputtering decreases when the substrate temperature during deposition is raised from room temperature and almost vanishes at 200 °C. At this temperature Pt (111) position almost reaches to the bulk two theta value of 39.75° deg of the strain free Pt (111) peak position [14]. For higher temperatures, the Pt (111) peak again moves towards smaller 2 theta values related to the swelling of the d_{111} spacing together with a loss of the crystalline quality (increased peak width). Interestingly, the peak position of the FTC deposited films remains constant for all substrate temperatures, although the strong increase of the peak height with substrate temperature indicates a substantial improvement of the crystalline quality at higher temperatures. The positions of the Pt peak and the out-of-plane strain values calculated from the shift of the peak relative to the position of the strain free Pt (111) peak are listed in Table 1.

Reciprocal space maps (RSMs) provide information on lattice imperfections such as strain or defect gradients together with compositional gradients for multi-element thin films. In this study, RSMs are recorded for a system consisting of a single Pt layer. Therefore, all observations apparent in RSMs can be attributed to the lattice imperfections of the Pt films. Similar to the XRD data shown in Fig. 1, all RSM data are normalized to the Al_2O_3 (0006) peak to facilitate the comparison of different samples. The RSM of the Pt layer grown by conventional magnetron sputtering on an unheated substrate (fig. 2 a) shows high intensity and a narrow distribution around the Pt (111) peak. This confirms the relatively good crystalline quality of the film deposited by conventional sputtering at room temperature that was also deduced from the presence of a reasonably narrow and intense Pt (111) peak observed in the conventional 2 theta scans. The symmetric and relatively narrow distribution around Pt (111) peak indicates a small spread of the tilt-mosaicity and strain gradient. The RSM data of the film grown at 400 °C by conventional magnetron shows a very small intensity (fig. 2b). At the first glance, the spread along the omega axis appears to be small. This apparently small width of the peak arises from low photon count caused by the poor crystalline quality and large mosaic spread. Again, this observation is in agreement with the low intensity of the Pt (111) peak, large peak width and large FWHM of the RC observed. The film deposited by FTC sput-

tering at RT shows broadening of the Pt (111) lattice point in the omega direction (fig. 2d), which indicates the spread of the mosaic blocks tilt in the out-of-plane direction. The narrow distribution in 2 theta direction and closer peak position to the theoretical value reveals the absence of strain in this film. The narrowest spread and a very symmetric distribution of the diffraction vector intensity both in the omega and 2 theta direction is observed for the film grown at 400 °C substrate temperature by FTC deposition (fig. 2e). Clearly, this film shows the best crystalline quality in terms of low mosaicity and smaller gradient of the out-of-plane strain when compared to the other samples prepared in this study.

Shown in Fig. 2 c) and f) are AFM images of the Pt films grown at 400 °C by conventional magnetron and FTC, respectively. Film sputtered by conventional magnetron sputtering show formation of large island-like features with trenches having depths that could reach the substrate. These trenches indicate the loss of film integrity and the start of Volmer-Weber growth mode confirming the observations of previous studies [15,16]. In contrast, the AFM image acquired on the FTC grown film display a flat surface (rms roughness below 0.35 nm) and no trenches are visible.

The epitaxial relation of the Pt film with the substrate is further investigated by performing pole figures. Fig. 3 shows the Pt (311) pole figure of the film grown by FTC at 400 °C substrate temperature. The pole figure was collected in a declination range between 0° and 80°. The Pt (311) peak in the pole figure is centered at $\psi=29.4^\circ$, as expected for a film oriented in (111) direction. The pole figure shows 6 narrow, point-like, high intensity poles surrounding the central area ($\chi = 0^\circ$). The observation of 6 poles confirms an epitaxial film growth with two in-plane orientations of the Pt crystallites which has also been observed in MBE-grown (111) Pt layers [5]. It is also worth noting that no poles were observed for the film grown at 400 °C by conventional sputtering for different alignments revealing that the film has a 111-texture but no epitaxy-related in-plane orientation of the crystallites.

The FTC deposited films showed an improved crystalline quality with increasing substrate temperature. At 400 °C, a flat, unstrained, high-quality epitaxial Pt film was obtained, as confirmed by AFM, pole figures and a narrow RC. The width of the RC is still wider than the reported values for epitaxial Pt films grown by MBE at higher temperatures [5]. Nevertheless, our results permit the conclusion that a relatively good epitaxial quality can be obtained also with FTC deposition but at a higher deposition rate than MBE. Improved film quality at elevated temperatures suggests that the quality could be further improved at even higher substrate temperatures. However, higher temperatures were not accessible with the experimental setup used here. In contrast, grown on unheated substrates, the FTC-deposited Pt film showed a very broad (111) peak and a wide RC indicating that the film consists of very small crystallites/grains with a 111-texture. Pt films with a much narrower Pt (111) peak were obtained also at room temperature but using conventional magnetron sputtering. This confirms that

Fig. 2. Reciprocal space maps of Pt films at around Pt(111) peak. Films grown by conventional sputtering at room temperature (a) and 400 °C (b) and FTC sputtering at room temperature (d) and 400 °C (e). Red dashed lines are placed to theoretical 2 theta position of Pt(111) peak to guide the eyes. Surface topography images of Pt films deposited at 400 °C by conventional sputtering (c) and FTC sputtering (f).

Fig. 3. Pole figure of Pt film grown at 400 °C by conventional FTC sputtering performed aligning on Pt(311) Bragg position.

the minimum adatom energy must be already available to promote the crystalline film growth for the conventional magnetron sputtering. A comparison of samples from both deposition types show that conventional magnetrons provide to adatoms a cumulative kinetic energy that match the effect of raising the substrate temperature. At substrate temperatures below 200 °C, the film grown by conventional magnetron show some degree of epitaxy. Above 200 °C, the energy supplied by conventional magnetrons is sufficient to trigger the start of a Volmer-Weber growth mode, as seen in AFM (Fig. 3 c). The island formation establishes a multiplicity of crystallite orientations [15,17] which causes the broadening of the RCs. Differences in the starting temperature of Volmer-Weber type growth compared to the published literature are attributed to the differences in the temperature calibration of each chamber, deposition power and different substrate-to-target distance [15].

Achieving lower adatom energies in conventional magnetron sputtering require either lower sputtering powers, which we kept at the minimum for our case or relatively high deposition pressures [18], wherein scattering during the transit from target to substrate moderates the adatom energy. But an undesired effect of this strategy is the increased defect concentration (i.e., larger pores, etc) and film roughness [19]. Consequently, evaporation methods such as molecular beam epitaxy (MBE) are preferred over sputtering for producing either nanocrystalline or epitaxial Pt layers [20]. Based on our results, it therefore appears that FTC deposition can produce films of characteristics closer to those grown by MBE [21], with clear advantages of note over the latter: FTC deposition rates are significantly higher than thermal evaporation sources [22] (for this study, the deposition rate was 0.09 nm/s) and UHV conditions are not necessary (deposition at 1.7 microbar and base pressures higher than 10^{-8} mbar). Both characteristics constitute a significant economic advantage and control flexibility.

13 nm thick Pt layers grown on Al_2O_3 (0001) substrates at different temperatures display different microstructures depending on the sputtering method. Conventional magnetron sputtering produces films with a limited degree of epitaxy, which become discontinuous due to Volmer-Weber growth modes at temperatures near 400 °C. In contrast, FTC sputtering provide low energy adatoms with which films grown at or below about 100 °C have very fine crystallites showing very low degree of out-of-plane ordering, and films grown between about 200 °C and 400 °C are epitaxial and devoid of cracks or islands. Access to the latter two types of microstructures by FTC techniques a priori constitutes a significant deposition time- and cost advantage over other alternatives, which provide low adatom energies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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