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Sputtered Ag thin films with modified morphologies: Influence on wetting property

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ABSTRACT

Silver thin films with thickness ranging from 3 nm to 33 nm were sputter deposited onto silicon wafers and tungsten layers. Those W layers were previously synthesized in the same DC magnetron sputter deposition system with various experimental conditions (argon pressure, target to substrate distance) in order to stabilize different surface morphologies. SEM observations and AFM images showed that the growth mode of Ag films is similar on Si substrates and on the smoothest W layers, whereas it is modified for rough W layers made of sharp grains. The effect of the W layer morphology on Ag film growth was clearly evidenced when the deposition took place at high temperature. It is seen that performing the deposition onto substrates of various morphologies allows tailoring the wetting property of the Ag deposit.

1. Introduction

It is well known that wetting properties of materials depend on their chemical nature and their roughness/morphology. The role of the surface roughness has widely been studied and it has been found to have opposite effects: increasing the roughness of a chemically hydrophobic surface will enhance its hydrophobicity, while increasing the roughness of a hydrophilic surface will further its hydrophilicity [1]. It has also been shown that surface state composed of superposition of two roughness patterns at different length scales, and fractal roughness may lead to superhydrophobicity, characterized by a contact angle higher than 150° [2]. Studies have been conducted on the roughness scales that would promote superhydrophobicity [3,4]. It has been found that nano-roughness associated to micro-patterns could promote this property, for instance by studying biological samples such as Lotus leaves [5]. This kind of multimodal roughness has been successfully obtained on various metal surfaces [6,7]. It is interesting to note that by properly texturing the surface, superhydrophobicity has been obtained on hydrophilic substrates, showing the major role played by the morphology on the wetting property [8].

Depending on the targeted application, hydrophobic or hydrophilic surfaces are requested. Hydrophilicity is preferred when strong interaction with aqueous media is necessary, like for example, antibacterial property or anti-fogging [9]. On hydrophilic surfaces the presence of a tightly adherent layer of water may help avoiding oil adsorption, like in anti-graffiti coatings [10]. Hydrophobicity and superhydrophobicity is associated to water repellency, anti-fouling, anti-adhesion and self-cleaning [11]. Usually for a surface to be self-cleaned a high static contact angle is not the only required parameter, a low sliding angle is also necessary, that means the contact angle hysteresis has to be low [9]. On this kind of surfaces, the droplets may roll in addition to slide, which facilitates removal of contaminant particles and waste, which are weakly link to the material [4].

However in some cases, a self-cleaning effect has been reported for superhydrophilic surfaces, like for TiO_2-based compounds [12]. Self-cleaning property of TiO_2 has been investigated by many authors and has been found to be also related to its photo-catalytic property [13,14]. Thanks to its superhydrophilicity, dusts and organic contaminants formed by UV decomposition of oils... etc. are able to be efficiently removed from the surface under rainwater, i.e. under a water flow.

In the aim to synthesize antibacterial and easy-to-clean coatings, the wetting property of magnetron sputtered Ag thin films deposited onto substrates exhibiting various morphologies was studied. Ag was chosen for its well-known broad-spectrum antibacterial ability, excellent biocompatibility and satisfactory stability [15–17]. The idea is to build a two-scale roughness, in order to further the removal of water that is used during the cleaning step in the targeted application.

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Magnetron sputter deposition was used among PVD techniques because most of the materials can be efficiently sputtered and many parameters can be varied (input power, gas pressure, target-substrate distance) to control the film properties. For instance, biasing the substrate would allow assisting the film growth by plasma ion bombardment, which is known to enhance the density and lower the roughness. High peak power impulses (HiPIMS) could also be used in order to induce ionization of the sputtered vapor, which could further broaden the accessible range of film characteristics.

In the preliminary study reported in this paper, conventional DC (direct current) magnetron sputtering was used to investigate, first, the growth of Ag on a flat silicon wafer, and second to synthesize W layers, that were used as textured substrates. W thin films deposited by magnetron sputtering have often been investigated [18–21]. W was chosen in the present work because, depending on the deposition conditions, films with very different features could be obtained, ranging from dense and flat to porous, columnar and rough [22,23]. Moreover it exhibits good hardness, which is one of the required properties, and has already been deposited in our sputtering apparatus [20]. The influence of the substrate morphology onto the Ag film characteristics was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Contact angle measurements were performed on Ag on Si (to study the intrinsic features of Ag films grown by magnetron sputtering), W on Si (to evidence wetting properties introduced by the sublayer) and Ag on W/Si (final two-scale roughness coatings) in order to evidence the parameters (surface roughness and/or chemistry effect) governing the wetting property.

To our knowledge, it is the first time that a stacking of layers is used to modify the wetting property of an antibacterial deposit in the aim to improve its cleaning efficiency.

2. Materials and methods

Ag films and W under-layers were deposited onto Si wafers by DC (direct current) magnetron sputtering of pure Ag (99.99%) and W (99.99%) 4″ target, respectively. The substrates (Si wafers and W/Si) were placed on a heatable-rotating substrate holder 12 cm away from the target, in a stainless steel vacuum chamber evacuated down to 10^{-4} Pa. Deposition conditions of silver remained unchanged throughout the study: Ar gas pressure was set to 2.5 Pa, and input power to 50 W. The deposition time was varied from 30 s to 5 min, corresponding to deposited thicknesses from about 3–33 nm. For thinnest deposited films, the thickness is calculated from the deposition rate determined on thickest films. In an attempt to investigate a wide range of Ag morphologies, deposition was also carried out at different temperatures: 230 and 400 °C.

In order to synthesize layers with various morphologies, sputtering of W was carried out at different Ar pressures (from 0.25 to 5 Pa) and target-to-substrate distances (11–12 cm). Both parameters (or $P \times d$) determine the number of collisions that sputtered W atoms undergo in the gas phase, which plays a role on their kinetic energy as they reach the substrate [20,22,23]. As often reported in literature for PVD techniques, the energy brought by depositing atoms influences the film structure [24–26]. This is especially the case for W, which has been found to form dense smooth films at low pressure and columnar, porous, rough films at high pressure. The input power during W sputter deposition, which is another parameter that could influence the film morphology [18,20], was set to 500 W in this study. Indeed, the aim of this work was not to perform a parametric study of W growth, but to synthesize W layers exhibiting a large range of morphologies. This was possible in our experimental configuration with a fixed power. Typical deposition time was 10 min, leading to layers of 300–800 nm thickness. These layers were used as substrates for the deposition of Ag thin films.

After deposition, the morphology of Ag on Si, W on Si and Ag on W/Si samples were analyzed using a FEG-SEM (Carl Zeiss SMT, Supra-40) and an AFM from Digital Instrument, Nanoscope III using silicon cantilevers (300 kHz). AFM images have been recorded using tapping mode. Only height images are displayed. RMS roughness was estimated using image analysis of the AFM 1 μm × 1 μm images. It is important to note that the aim here is to correlate a parameter standing for the surface morphology to the wetting properties of the samples rather than determining a true value of the roughness RMS. X ray diffraction (Brüker D8 Advance, λ_{Cu} = 1.5606 Å) in θ–2θ configuration was also carried out on W layers, in order to completely characterize the substrates on which Ag will be deposited. Static contact angle measurements were performed using a Digidrop apparatus from GBX (http://www.gbxonline.com/). A 2 μl distilled water drop was deposited onto the surface and the contact angle was determined by analysis of the recorded images using ImageTool software (http://imagetool.software.informer.com/). Three measurements were done on each sample.

3. Results and discussion

3.1. Ag growth onto Si wafer

In a first run of experiments, Ag was sputter deposited onto the flat surface of Si wafers. Films from 3, 6, 16 to 33 nm in thickness have been synthesized; corresponding SEM and AFM images are shown on Fig. 1. 3 and 6 nm thick thin films (Fig. 1a and b) appear continuous on both SEM and AFM images, and a tiny fine structure is visible, close to SEM resolution, reason why the 3 nm thick film could not be imaged by this technique. It seems that the Ag deposit completely wet the Si wafer. On the 16 nm thick film (Fig. 1c), particles of various sizes and shapes are visible, and the 33 nm thick film is composed of 25–30 nm spherical particles (Fig. 1d). Very good agreement is found between SEM and AFM analyses.

From the above observations it appears that a change occurs in the growth mode of silver between 6 nm and 16 nm thick films. It turns from the covering of the substrate by a wetting Ag film (2D layer), to the formation of 3D islands. This kind of Stranski–Krastanov mode has already been observed for Ag growth on substrates of different kinds: Si (0 0 1) [27] and ZrNiCuAl metallic glass [28]. In this second study, 3D islands are detected above 6 ML, i.e. for thicknesses above 11 nm, which is in good agreement with our results, since we observed 3D islands for 16 nm thick film. Jing et al. evidenced that 3D islands are composed of several fragments indicating the presence of grain boundaries, which suggests that they are polycrystalline [28]. The same kind of observation can be made on AFM images of both 16 and 33 nm thick films in the present work in Fig. 1.

On 16 nm thick film (Fig. 1c), 100 nm clusters exist with smaller ones of various sizes and shapes, which is very different from what is seen on the 6 nm thick film. Moreover, voids seem to appear between smallest clusters, and the roughness that was very low before (0.6 nm on 3 and 6 nm thick films) increases up to 2.1 nm. Clearly the homogeneous 2D layer present on previous films seems to be completely modified. Same kind of morphology has been reported by Polop et al. [29] in their study of Ag growth on amorphous silicon in the same range of thickness (16 nm). This could be explained by the unwetting of the previously formed 2D layer. It has been reported that, in some cases, this 2D layer becomes unstable when the 3D islands start to grow. This has been explained by the fact that some of the Ag atoms leave the 2D layer and go into the 3D islands, exposing area of the original substrate [27]. In the