Materials Science and Engineering C 74 (2017) 536–541

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Antibacterial activity of microstructured sacrificial anode thin films by combination of silver with platinum group elements (platinum, palladium, iridium)

Keywords:
Sacrificial anode
Antibacterial surface
Titanium
Silver
Platinum
Palladium
Iridium
Thin film

1. Introduction

Infections related to medical devices and implants cause constant and serious clinical problems [1]. Bacteria can adhere to and colonize the surfaces of various biomaterials. Uncontrolled bacterial growth may result in formation of bacterial biofilms which protect the microorganisms against host defense mechanisms and make antibiotic treatments difficult if not ineffective [2,3]. In general, an infected implant can lead to serious consequences including revision surgery, tissue debridement, and prolonged antibacterial treatment [4]. Therefore, the development of biomaterials with antibacterial surfaces which hinder or prevent bacterial colonization and growth is an important challenge in biomaterial research. The inhibition of an initial bacterial colonization avoids most implant-related infections and reduces the chance of biofilm formation [5]. Many strategies have been followed to inhibit initial bacterial colonization on the surface, either by surface topography [6] or by special coatings [7]. These include the use of various silver (Ag) coatings e.g. [8] due to their broad anti-bacterial activity (both gram-negative and positive bacteria) and a low incidence to induce bacterial resistance [7].

The oxidative dissolution of Ag releases Ag ions (Ag^+) which induce the antimicrobial activity [9,10]. Accordingly, the antibacterial activity could be controlled by adjusting the Ag^+-release [11]. Generally, this could be achieved by Ag-nanoparticles (nanosilver) which have an increased surface area. However, the exposure to nanosilver may induce additional risks for medical application such as unwanted tissue reactions [12]. This prompted us to study an alternative mechanism to enhance Ag ion release by the use of the sacrificial anode principle for thin film systems consisting of microstructured Ag films coated on a more noble base layer, i.e. gold or Pt-group elements. Sacrificial anodes are widespread in technical applications (e.g. protection of ferrous ship hulls or water heaters by zinc parts). Generally, when two electrochemically different metals (or alloys) exist in an electrolytic environment, the less noble (electrochemically more active) metal protects the more noble one by corroding, it is sacrificed in favor of the more noble part [13]. However, this approach has not received much attention in thin film and biomedical research areas.

It was reported that a weak direct electrical current induced anodical polarization of Ag electrodes and led to a better antibacterial effect [14]. A comparable improved anti-bacterial activity was demonstrated for Ag-coated Ti screws which were energized by weak direct current and then prevented implant-associated deep bone infections in an animal model [15]. For biomedical applications it would be more suitable to induce the anodical polarization of Ag using specific metal combinations. For the combination with Ag as the sacrificial anode, only a few other more noble metals are suitable such as gold (Au) or platinum (Pt). In one example, Dowling et al. reported the enhanced antibacterial activity of an Ag-Pt alloy in comparison with pure Ag [16]. There is a commercially available coating using Ag, Pd and Au particles which are chemically bonded to surfaces (Bactiguard AB, Stockholm, Sweden). There is also a patent indicating enhanced antibacterial activity of medical devices using sacrificial anode systems like Pt/Ag, Al/Ag, Al/Au, Al/Pt [17].

Recently we successfully proved the sacrificial anode principle by the combination of thin film Ag dot arrays on a thin Au film [18]. We demonstrated that Ag on Au corrodes much faster than Ag on Ti. This created an enhanced antimicrobial activity compared to a system consisting of Ag and the less noble metal Ti. Thus, the objective of this study is to implement elements of the Pt-group for a comparable sacrificial anode principle using thin base films of platinum (Pt), palladium (Pd) and iridium (Ir) in combination with thin film Ag dots to access antibacterial activity and inhibition of bacterial attachment and growth. For this evaluation five different Ag dot arrays (single dot diameter: 20 μm) with varying periodicity (16, 64, 144, 256 and 400 dots/mm^2) were fabricated on top of continuous Pt, Pd, Ir or Ti thin films by magnetron sputter deposition and photolithographic patterning. The schematic of Ag dot arrays fabricated on the thin film layers and the processing steps are shown in Fig. 1.

2. Materials and methods

2.1. Sample fabrication

All samples (Fig. 1A, 6.5 mm × 6.5 mm) were fabricated by magnetron sputter deposition along with a photolithographic process. All sputter depositions were performed under a base pressure $\leq 1 \times 10^{-6}$ P as on oxidized Si(100) substrates (with 1.5 μm thick thermally oxidized layer serving as a diffusion barrier). Fig. 1B shows a schematic of the sample fabrication process including layer depositions and the photolithographic patterning process. In the first step (see Fig. 1B (a)), Pt, Pd, Ir and Ti thin films (thickness ≈100 nm) were individually deposited on Si/SiO_2 substrates.

The films were deposited at room temperature in a sputter system (AJA ATC-2200V sputter system) by sputtering of 4-inch diameter Pt (99.99% pure, FHR Co.), Pd (99.99% FHR Co.), Ir (99.90% pure, EvoChem. Co.), and Ti (99.995% pure, KJ Lesker Co.) targets. The depositions were

http://dx.doi.org/10.1016/j.msec.2016.12.075

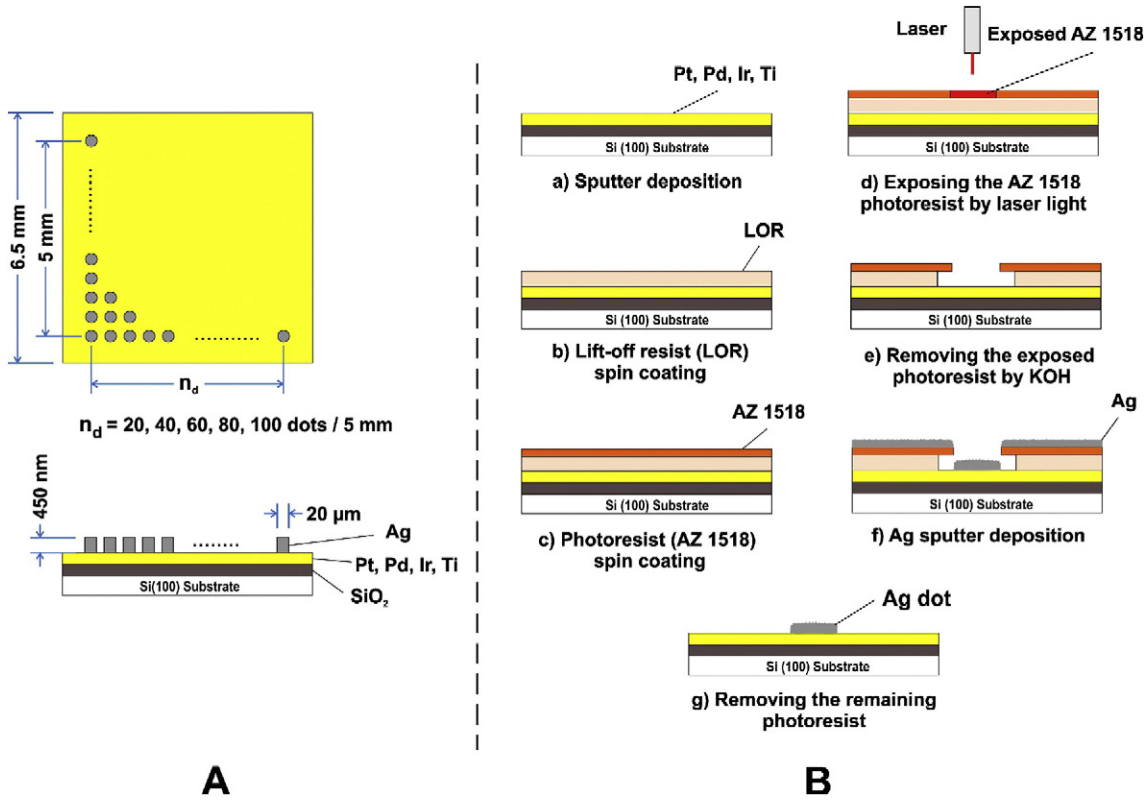

Fig. 1. (A) Design of fabricated dot arrays; B (a–g) Fabrication process of Ag dot arrays on continuous Pt, Pd, Ir and Ti thin films.

performed at an Ar working gas pressure of 0.67 Pa on a rotating substrate. The sputter powers (DC) for Pt, Pd, Ir and Ti were 59 W, 60 W, 59 W and 300 W, respectively. Subsequently, the substrates were spin-coated with a non-photosensitive layer of lift-off resist (LOR, MicroChem, Newton, MA, USA) (Fig. 1B (b)) and a photosensitive resist (AZ1518, MicroChemicals, Germany) (Fig. 1B (c)). After designing of specific dot patterns using Clewin software, the desired dot array pattern was exposed by a diode laser with a wavelength of 405 nm (Fig.

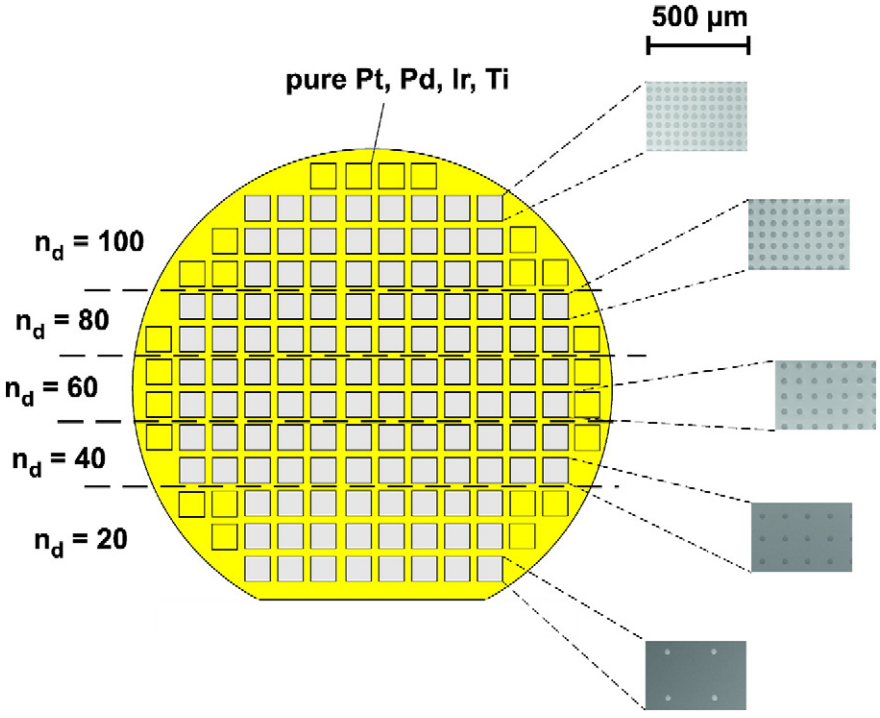

Fig. 2. Ag dot patterns with various types differing in dot density (n_d = 16, 64, 144, 256, 400/mm^2) and corresponding dots per row and column n_d = 20, 40, 60, 80 and 100 fabricated on a 4-inch Si wafer. The yellow squares at the sides of the wafer are presenting the pure Pt, Pd, Ir and Ti samples. The SEM images for each type of the samples were depicted at the right side of this figure.