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# Surface-enhanced Raman scattering substrates of flat and wrinkly titanium nitride thin films by sputter deposition

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ABSTRACT

Titanium nitride (TiN) thin films were prepared by RF magnetron sputtering on a bare Si surface and a silicone-oil-covered Si surface as surface-enhanced Raman scattering (SERS) substrates. The TiN film deposited on the bare Si surface had a flat surface with densely packed grains measuring 18 nm in diameter, whereas the TiN film deposited on the oil surface had a wrinkly pattern made of grains measuring 19 nm in diameter. To analyze the SERS effect, Rhodamine 6G (R6G) was used as a Raman probe molecule at various concentrations ranging from $10^{-4}$ to $10^{-8}$ M. The analytical enhancement factor (AEF) values at $10^{-6}$ M R6G were respectively $6.2 \times 10^3$ and $1.3 \times 10^4$ for the flat TiN film and wrinkly TiN film. The SERS effect could be attributed to the enhancement of the local electromagnetic field at the top of the nano-sized grains. The wrinkly TiN film had a higher AEF than the flat TiN film, possibly due to the increased area of the Raman active spots. The wrinkly TiN film exhibited high level of SERS activity and achieved an R6G detection limit of $10^{-8}$ M.

## 1. Introduction

Titanium nitride (TiN) attracted considerable attention due to its unique thermal, chemical and mechanical stability. TiN exhibits the optical and electrical properties of metals [1–6]. Nanostructures of noble metals like Au and Ag have been used in various applications based on plasmon resonance [7]. Previous reports have shown that TiN thin films have optical properties similar to Au, and the permittivities of TiN in real part of visible and IR are negative, resulting in resonant plasmon characteristics [3]. Hence TiN has been considered an alternative to noble metals for use in plasmonic devices [3,8]. Moreover, TiN is inexpensive, hard, biocompatible and hemocompatible, and has the been successfully used in many biomedical devices and sensors [9,10].

Surface-enhanced Raman spectroscopy (SERS) has attracted interest following the discovery of the surface-enhance Raman effect for pyridine adsorbed on Ag surfaces [11,12]. SERS can reliably detect single molecules [11,12]. A theoretical explanation of the Raman signal enhancement is as follows. First, when electrons in metals resonate with the incident photons via enhancement of the local electromagnetic (EM) field, they produce enhanced Raman scattering from the Raman probe molecules close to the metal surface [13,14]. Secondly, when Raman probe molecules are present on the active sites of metals, a charge transfer process may occur between the molecules and the metal surface [15]. Metallic nanostructures such as nanoparticles, islands, rough surfaces, fractals, and arrays of nanoscale objects enhance the EM field in the region of high curvature, resulting in high SERS intensity [16,17]. Extraordinary enhancement of the EM field and SERS intensity also occur in 'hot spots' or the nanoscale gaps between metal objects [18]. The surfaces of noble metals such as Au and Ag exhibit strong plasmon resonance producing a high surface-enhanced Raman effect [19,20]. However, noble metals are expensive and have poor biocompatibility, raising the need to develop alternative materials for plasmonic applications [4]. For instance, nanostructures of several oxides such as $TiO_2$, $Fe_2O_3$, $SnO_2$, ZnO and tin-doped-indium oxide (ITO) have been fabricated to demonstrate surface-enhanced Raman effect [21–25]. Recently, SERS of TiN with various morphologies have been demonstrated. For example, a non-continuous TiN thin film exhibited a 40% increase in Raman intensity of the Si substrate underneath [26]. A continuous TiN thin film prepared by sputter deposition has been used as a SERS substrate to magnify the Raman intensity of Rhodamine 6G (R6G), which is commonly used as a Raman probe molecule [27]. A random array of TiN nanorods produced by sequential hydrothermal and nitriding processes showed a SERS enhancement

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factor of 8900 for R6G of $10^{-5}$ M [28]. Rough TiN films produced by nitriding sol-gel-derived $TiO_2$ films showed SERS enhancement factors of 4100 to 10,600 for R6G of $10^{-6}$ M [29–31].

To achieve a strong Raman enhancement effect, various metal nanostructures with high "hot spot" densities have been produced for use as SERS substrates including island films, porous films, nanoparticles, nanowires, nanorods and dendrites [18,32]. Few reports have focused on wrinkly Ag- and Au-based SERS substrates [33–41]. SERS substrates with wrinkle patterns can be formed by laser irradiation of Si surfaces coated with a thin Au film or Si surfaces immersed in an $AgNO_3$ solution [33,34]. Wrinkly SERS substrates can also be generated by depositing Ag or Au on wrinkly templates [35,36]. SERS substrates with wrinkly Ag and Au nanostructures can also be produced by buckling flat Ag and Au films on pre-strained polymer substrates after releasing the strain [37–41]. On the other hand, wrinkly films have been formed on liquid surfaces through the relief of residual stress [42]. In that approach, silicone oil, with a vapor pressure less than $10^{-6}$ Pa, is commonly used as a liquid substrate for the vacuum deposition of metal wrinkles [43–48]. Because flat TiN films are commonly prepared by reactive sputter deposition on solid substrates, we expect that wrinkly TiN films can be produced by reactive sputter deposition on liquid substrates.

In this work we prepared TiN films by reactive sputter deposition onto a silicone oil-coated Si substrate and obtained a wrinkled morphology. The resulting wrinkly TiN film was compared with flat TiN film deposited on a blank Si substrate for SERS study using R6G as the Raman probe molecule. Raman intensity enhancement was demonstrated on both the flat and wrinkly TiN films.

## 2. Experimental

Flat and wrinkly TiN films were prepared on Si (100) substrates by RF magnetron sputtering of a Ti (99.99%) target in a mixed flow of 15 $cm^3$/min Ar (99.999%) and 2 $cm^3$/min $N_2$ (99.999%). The base pressure of the sputtering system was $2.7 \times 10^{-4}$ Pa and the working pressure was 1.2 Pa. Prior to depositing flat TiN, bare Si substrates were cleaned by sonication with acetone followed by isopropyl alcohol and deionized water. The substrate temperature was increased to about 80 °C during deposition of the flat TiN film for 20 min. For the preparation of wrinkly TiN films, a thin layer of silicone oil (D-31, ULVAC) was deposited on the cleaned Si substrate to form a liquid substrate by thermal evaporation in air in advance. The thickness of the silicone oil film on the Si substrate was determined to be 48 nm by ellipsometry using a 632.8 nm light source. During the deposition of the wrinkly TiN film for 30 min, the substrate temperature was increased to about 100 °C. After depositing TiN on the liquid substrate, the silicone oil was evaporated away in a vacuum furnace at 170 °C for 180 min, and a wrinkly TiN film was generated on the surface of the Si substrate.

The morphology of the TiN films was inspected by field emission scanning electron microscopy (FESEM, JSM-6500F, JEOL). The mean grain size of TiN thin films was measured using ImageJ software. The crystal structure of the TiN films was characterized by X-ray diffractometer (XRD, D8 Advance, Bruker AXS). The permittivities of the flat TiN film and the thickness of the silicone oil on the Si substrates were obtained using a spectral ellipsometer (M-2000VI, J.A. Woolam). To characterize the SERS effect of the TiN films, Rhodamine 6 G (R6G, 99%) was used as a Raman probe molecule and the Raman spectra of the R6G-coated TiN were recorded using a Raman spectrometer (iHR550 HORIBA). All the Raman measurements were carried out using a 532 nm laser source through a 50× objective lens, with a power density of 500 mW/$cm^2$, with 30 accumulations and 1 s acquisition time.

To evaluate the performance of the TiN SERS substrates, R6G solutions of $10^{-4}$ to $10^{-8}$ M were prepared in deionized water. TiN samples were immersed in the R6G solutions for 1 h to soak R6G molecules. The TiN samples were then removed from the R6G solutions, gently blown with $N_2$, and dried in air for 1 h. To evaluate the Raman enhancement factor (EF) of the TiN samples, a reference sample was prepared by soaking $10^{-2}$ M R6G on a blank Si substrate followed by blowing with $N_2$ and air drying.

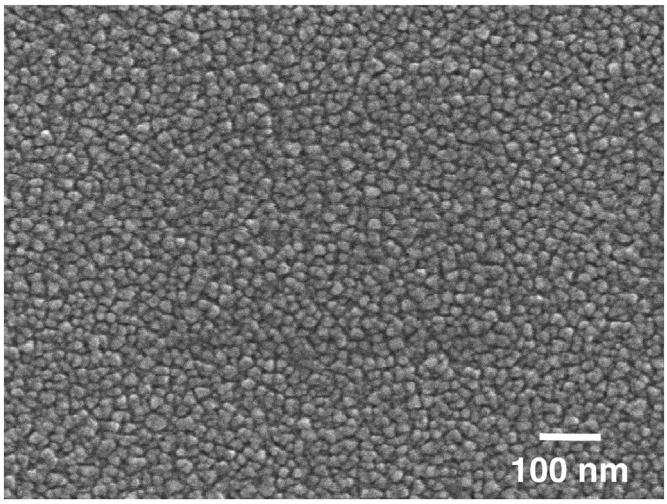


**Fig. 1.** SEM top view image of the flat TiN film.

## 3. Results and discussion

Fig. 1 shows the top view SEM image of the TiN thin film directly deposited on a bare Si substrate. The TiN film is flat and denoted as TiN-F hereafter. The flat TiN film is about 60 nm thick and has a granular morphology with a mean grain size of 18 nm. Contrarily, as shown in Fig. 2, the TiN film deposited on a liquid substrate presents uniform wrinkled patterns after the silicone oil is evaporated, and is denoted as TiN-W. The TiN-W film is about 60 nm thick and the average periodicity wavelength of the hierarchical wrinkles is around 80 nm, as shown in Fig. 2. Meanwhile, the TiN-W film is also composed of granules with a mean grain size of 19 nm. As a result, a flat TiN film was obtained by reactive sputter deposition of TiN on the bare Si substrate, whereas a wrinkly TiN film was generated by depositing TiN on a silicone oil surface. Wrinkly metal films have been produced on silicone oil surfaces by thermal evaporation and sputter deposition [42–48]. The temperature of the silicone oil rises during metal deposition and metal wrinkles are derived through the relief of compressive stress during the cooling of the metal/oil systems [45,46]. Herein, we demonstrate that TiN wrinkles can be produced by depositing TiN on a silicone oil surface by

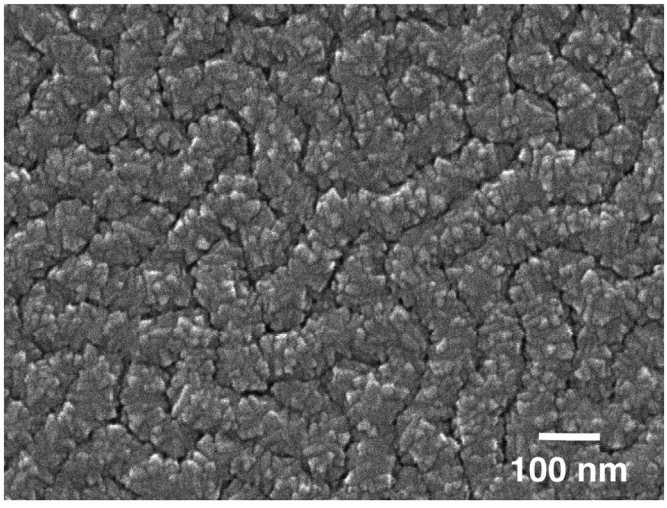


**Fig. 2.** SEM top view image of the wrinkly TiN film.

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