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Study of the effect of plasma current density on the formation of titanium nitride and titanium oxynitride thin films prepared by reactive DC magnetron sputtering

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ABSTRACT

Titanium nitride and titanium oxynitride films were deposited by varying the plasma current density from 10 mA/cm^2 to 40 mA/cm^2 using DC magnetron sputtering at constant gas flow rate and deposition time. Samples were characterized by Grazing Incidence X-Ray Diffraction, XPS, Nanoindentation and colorimetric analysis. Different coloured films like golden, blue, pink and green were obtained at different current densities. At lower current density (10 mA/cm^2), golden coloured stoichiometric titanium nitride film was formed. At higher current densities (20, 30 and 40 mA/cm^2), non stoichiometric Titanium oxynitride films of colour blue, pink and green were formed respectively. The thickness of the films increased with plasma current density from 43 nm to 117 nm. It was found that the colour variation was not only due to thickness of the film but also due to oxygen atoms replacing the nitrogen positions in TiN lattice. Hardness and Young Modulus of the films were found to decrease from 17.49 GPa to 7.05 GPa and 319.58 GPa–246.77 GPa respectively with increasing plasma current density. This variation of hardness and Young Modulus of the films can be speculated due to change in crystal orientation caused by oxygen incorporation in the films. The film resistivity increased from 16.46×10^{-4} to 3.28×10^{-1} Ω cm for increasing plasma current density caused due to oxygen incorporation in the crystal lattice.

1. Introduction

TiN films due to its hardness, properties of barrier diffusion, chemical stability and attractive colours have gained importance in wide range of applications like cutting tools, MEMS, solar reflector and decorative coating etc. [1–5]. Titanium nitride and titanium oxynitride coloured films are attracted due to its consumer demands in ornament industries [6]. These films have been prepared by various chemical & physical deposition techniques but mass production of coloured films at short interval is a challenging task for this industry. Titanium nitride and oxynitride film is not only important for its colour but also important for electrical properties at interface between two layers. Recent work on titanium nitride films show low electrical resistivity and also good ohmic contacts to silicon [7–9], whereas titanium oxynitride films provide a retarding diffusion barrier at the interface between a metal and silicon. It mainly occurs due to blocking of fast diffusion path by oxygen, which is leaving strong influence on the barrier performance [10]. If we could control the amount of oxygen inside the titanium nitride film, it will fulfill to the desired requirement in different industries. Hence in this work one attempt has been made to incorporate oxygen in TiN film.

Literature indicates that mechanical properties, electrical properties and colours of the TiN film mostly depend on film thickness and oxygen content in the film [11–14]. A number of reports are available on the deposition of TiN & TiON films obtained by different plasma parameters. But a very few reports are available on deposition of titanium nitrides in presence of a very small amount of oxygen at deferent plasma current density.

In the present paper attempts has been made to deposit titanium nitride and oxynitride thin films under trace of oxygen available in deposition chamber using DC magnetron sputtering. The plasma current density was varied from 10 mA/cm^2 to 40 mA/cm^2, at constant gas flow rate of (Ar: N_2) and a small incorporation of oxygen for a constant deposition time. The hardness, colour and resistivity of the deposited films could be controlled by varying the plasma current density.

2. Experimental details

2.1. Deposition

A schematic diagram of the DC magnetron sputtering deposition system is shown in Fig. 1. This system consists of a vacuum chamber,

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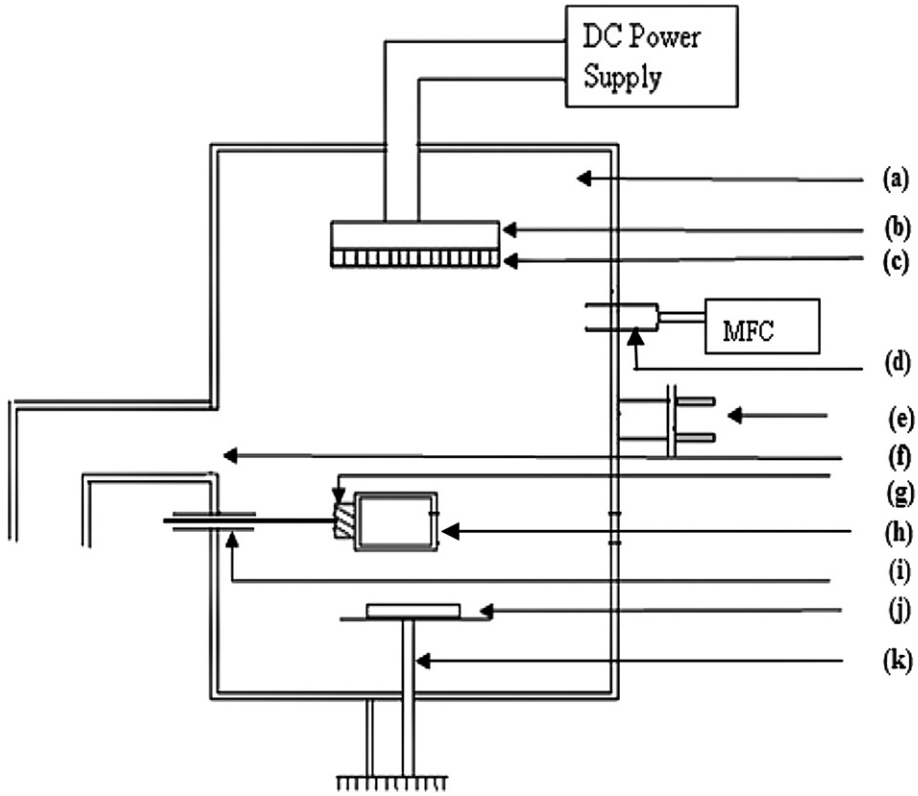

Fig. 1. Schematic Diagram of DC magnetron sputtering system (a) Vacuum chamber (b) Cathode (c) Target (d) Gas inlet through MFC (e) Pirani and Penning Gauge (f) Connected to rotary and diffusion pump (g) Insulation (h) Faraday Cup (i) Wilson seal (j) Substrate and (k) Substrate holder.

cathode, mass flow controller, sample holder, Faraday Cup and view port. Pure Ti target of size 50 mm diameters, 5 mm thick, was mechanically clamped to the magnetron cathode of the sputtering system.

Silicon substrates of size 10×10 mm^2 were obtained by cutting silicon wafers of thickness ~0.5 mm. The substrates were ultrasonically cleaned and dried at room temperature prior to deposition. Silicon substrates were mounted on the sample holder and evacuated upto a base pressure of $\sim 10^{-6}$ mbar. The surface of the target was sputter etched by Ar at 100 W for 20 min to avoid contamination prior to deposition. After sputter cleaning, the argon, nitrogen and oxygen gas flow rate was maintained at 14 sccm, 6 sccm and 0.5 sccm respectively. The deposition was carried out at working pressure of $\sim 2 \times 10^{-2}$ mbar and deposition time of 1 h. In this way, four films were obtained at four different plasma current densities (10, 20, 30, 40 mA/cm^2) and constant deposition time and gas flow rates. The deposition conditions are shown in Table 1.

2.2. Measurements

2.2.1. Plasma current density

A special type of arrangement was made to measure plasma current density just before the deposition. In this arrangement a metallic rod is mounted to one end of a ceramic plate and the other end was fitted to the Faraday cup of size 20 mm × 20 mm. This ceramic plate was used to electrical isolate (electrical) Faraday cup from metallic rod. The metallic rod is passed through the Wilson seal, which is connected to one port of the deposited chamber. Before deposition, the faraday cup was aligned to plasma zone to record plasma current density. The schematic diagram of the arrangement is shown in Fig. 1.

2.2.2. Crystallinity

Crystallographic analysis of the deposited films was done by GIXRD (Model: PAN analytical X'Pertpro 3040/60). X-ray from CuK$_\alpha$ (wavelength 0.154 nm) was used for the measurement and operated in Bragg-Brentano geometry. GIXRD spectra of the deposited films are shown in Fig. 1.

2.2.3. Chemical compositions

XPS analysis was performed using an Omicron EIS2000, employing a hemispherical analyzer. The analyzer was operated in the constant analyzer energy (CAE) mode. The pass energy was kept at 50 and 25 eV for wide and narrow scans, and the scanning steps was 0.2 eV. The incident radiation was un-monochromated MgKα (1253.6 eV), the source running respectively at conditions of 15 KV and 20 mA. Ar^+ ion beam etching was performed using a standard ionization gun operating at 1500 eV incident energy and

Table 1
Deposition Parameters for TiN (D.C. reactive Sputtering).

Objects	Specification
Target	Ti pure (99.99%)
Substrate	Si wafer
Target to substrate distance	6.5 cm
Base pressure	1.0×10^{-6} mbar
Operating pressure	2×10^{-2} mbar
Argon	14 sccm
Nitrogen	6 sccm
Oxygen	0.5 sccm
Current density	10, 20, 30 and 40 mA/cm^2
Substrate temperature	Room Temperature, no external heating was provided
Deposition time	1 h