Investigation of electrical and optical properties of low temperature titanium nitride grown by rf-magnetron sputtering

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Abstract. Titanium nitride is a promising material due to its low resistivity, high hardness and chemical inertness. Titanium nitride (TiN) can be applied as an ohmic contact for n-GaN and rectifying contact for p-GaN and also as a part of perovskite solar cell. A technology of TiN low temperature reactive rf-magnetron sputtering has been developed. Electrical and optical properties of titanium nitride were studied as a function of the rf-power and gas mixture composition. Reflectance and transmittance spectra were measured. Cross-section and surface SEM image were obtained. 250 nm thin films of TiN with a resistivity of 23.6 µOm cm were obtained by rf-magnetron sputtering at low temperature.

1. Introduction
Titanium nitride is a promising material due to its low resistivity, high hardness and chemical inertness. Titanium nitride is used in optical filters, thin film resistors, protective and decorative coatings. Titanium nitride can be applied as an ohmic contact for n-GaN and rectifying contact for p-GaN and also as a part of perovskite solar cell.

Most scientific articles reports dc-magnetron sputtering at 300-400 °C [3-5] or rf-reactive magnetron sputtering in 100% nitrogen atmosphere [6]. Heating up to 600 °C is used for obtain good stoichiometry of TiN. In this work we have reported low temperature rf-magnetron sputtering of titanium nitride.

2. Experimental details
TiN thin layers are generally deposited by rf-magnetron sputtering on glass and silicon substrates. Before the deposition – vacuum chamber was pumped off to a pressure of 6·10\textsuperscript{-6} mBar. Operating temperature in the chamber was 40-50 °C. \textsuperscript{14}N\textsubscript{2} and Ar were used as working gases. Optical reflectance and transmittance spectra were measured by spectrometer based on a SOLAR LS M266 monochromator. The morphology of the films was studied by SEM.

3. Results and Discussions
Reactive sputtering of titanium nitride means the use of metal target as the supplier of titanium and the mixture of reactive and working gases. TiN growth conditions require \textsuperscript{14}N\textsubscript{2}/Ar gas flow ratio of less than 1. The nitrogen flow should not be too small, otherwise the titanium will settle on substrate as nitrogen will not be sufficient for a reaction with titanium. If nitrogen flow is too much, it also becomes a working gas and only titanium growth begins on substrate.

The growth rate of TiN reactive sputtered film linearly increases with increase of rf-magnetron power. At the same time, the relationship between sputtering rate and \textsuperscript{14}N\textsubscript{2}/Ar ratio (figure 1) or
chamber pressure (figure 2) nonlinear. Thus a high concentration of gas molecules prevents sputtered particles of titanium, nitrogen and titanium nitride from settling to the surface of the sample. The growth rate of TiN on Si may reach maximum saturation at low N$_2$ concentration [4]. In this study, it was not observed.

Figure 1. The relationship between TiN deposition rate on Si and N$_2$/Ar ratio, rf-power of 400 W and 2·10$^{-3}$ mBar gas pressure.

Figure 2. The relationship between TiN deposition rate on Si and chamber pressure at rf-power of 400 W and N$_2$/Ar = 1/3 ratio.

SEM images of 300 nm TiN film sputtered on Si substrate show nano-crystal structure. All produced films with different thickness demonstrate smooth surface morphology (figure 3 and figure 4). The resulting films have flat surface with a metallic luster. TiN stoichiometry depends on N$_2$ concentration [4], therefore there is a difference in the structure of the two samples. Morphological studies showed the presence in films of nanoscale structures with a particle size of 16-38 nm.

Figure 3. SEM images of 300 nm TiN film on Si sputtered at rf-power of 400 W, 1/3 N$_2$/Ar gas ratio.
Figure 4. SEM images of 90 nm TiN film on Si sputtered at rf-power of 300 W, 3/4 N₂/Ar gas ratio.

Transmittance and reflectance spectra of produced films are shown on figure 5. These data well correlate with the other references [1,2]. Films exhibit a low reflection band in 350–600 nm. At the same time, no transmittance in visible range were observed. TiN films demonstrate golden colored mirror surface.

Figure 5. Transmittance and reflectance spectra of TiN with different films thickness

Resistivity of TiN films depends on the growth conditions. It's shown in table. Better resistivity was obtained with rf-power of 400 W N₂/Ar gas flow ratio 0.33. 252 nm thick film has a resistivity 23.6 µΩm cm that corresponds to the thicker TiN coatings [3]. First of all the resistivity depends on stoichiometry, which differ for various N₂/Ar ratio value [4], and on film thickness [5]. Actually, resistivity of 100-120 nm thin film 4 times more than 250-300 nm TiN film. As for the stoichiometric coefficient, a better resistance is achieved for N:Ti ratio of 0.98.
4. Conclusion
In this work we have reported low temperature rf-magnetron sputtering of titanium nitride. As a result 250 nm thin films of TiN with a resistivity of 23.6 µOm·cm and smooth surface morphology were obtained.

References
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