Lateral variation of target poisoning during reactive magnetron sputtering

D. Güttler, R. Grötzhel, and W. Möller

Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

(Received 11 May 2007; accepted 1 June 2007; published online 26 June 2007)

The reactive gas incorporation into a Ti sputter target has been investigated using laterally resolving ion beam analysis during dc magnetron deposition of TiN in an Ar/N₂ atmosphere. At sufficiently low reactive gas flow, the nitrogen incorporation exhibits a pronounced lateral variation, with a lower areal density in the target racetrack compared to the target center and edge. The findings are reproduced by model calculations. In the racetrack, the balance of reactive gas injection and sputter erosion is shifted toward erosion. The injection of nitrogen is dominated by combined molecular adsorption and recoil implantation versus direct ion implantation. © 2007 American Institute of Physics. [DOI: 10.1063/1.2752019]

Magnetron sputtering is a common technique in the fabrication of high quality functional thin films. In the reactive deposition mode, a metal target is exposed to a rare gas discharge to which a fraction of reactive gas (such as nitrogen and oxygen) is added. At the substrate, the reactive gas reacts with the sputtered target material to the desired compound. Its stoichiometry depends, e.g., on the reactive gas partial pressure and the deposition power. The efficiency of the process, however, is often limited by the so-called target poisoning, which means that the compound layer forms not only on the substrate as desired but also on the sputter target. This results in a significantly reduced sputter yield, and thereby a reduced deposition rate. As a further consequence, the reactive gas consumption decreases due to the lower yield of sputtered material, and its partial pressure increases rapidly. For this situation, global particle-balance models of the interaction between gas flow, target erosion, and thin film deposition show a partly negative slope of the relation between reactive gas flow and partial pressure, which results in a hysteresis behavior. A corresponding instability often requires additional means of stabilization for practical applications. At the target, the particle balance is determined by the fluxes of neutral and ionic species from the gas and the plasma. The incorporation of reactive gas has been suggested to result from a stationary balance of injection by ion implantation and chemisorption in connection with recoil implantation, and erosion by ion-induced sputtering. This was confirmed in previous experiments using in situ real-time ion beam analysis of the nitrogen incorporation at the target.

Magnetron discharges are laterally strongly nonuniform due to the electron confinement in the magnetic field configuration. In front of a cylindrical magnetron target a toroidal region of high plasma density is formed, which creates the so-called racetrack as a zone of high target erosion. Consequently, also a nonuniform incorporation of reactive gas atoms can be expected. With this background, an experiment has been designed, which allows laterally resolved in situ ion beam analysis of the reactive gas incorporation at the target surface. A standard magnetron sputter configuration was installed in an ultrahigh vacuum chamber of 50 l volume. The planar, cylindrical dc magnetron of 5 cm diameter was equipped with a 99.995% purity titanium target and installed in the center of an ultrahigh vacuum chamber of 50 l volume. It was operated in constant current mode at 0.3 A. Using mass flow controllers, the argon and nitrogen flows were fixed at 10 SCCM (SCCM denotes cubic centimeter per minute at STP) and varied between 0 and 2.5 SCCM, respectively, which resulted in operating pressures between 0.3 and 0.35 Pa. The partial pressures were measured by means of a mass spectrometer, which was calibrated in pure Ar and N₂. The target voltage adjusted from ~330 to ~360 V at increasing reactive gas flow. For in situ ion beam analysis of the nitrogen incorporation at the target by means of the ¹⁴N(d, α)¹²C nuclear reaction, the setup is attached to the beam line system of a 5 MV tandem ion accelerator (for details, see Ref. 10). The ion beam is collimated to a spot of 1 × 1 mm², which defines the lateral resolution of the analysis. The low cross section of the reaction requires analysis times of up to 30 min to obtain statistically satisfactory results. In order to reduce the consumption of the sputter target and the corresponding contamination of the target chamber, the measurements have been performed after magnetron operation. By comparison to real-time analysis during magnetron operation, it was assured that no postoperation nitrogen loss occurs.

Figure 1(a) shows the radial distribution of the ion current density across the target surface, which has been derived from the surface erosion profile after long-time operation for 17 h with Ar inert gas only. The current density varies between about 1 and 50 mA/cm² at the target center and the centerline of the racetrack, respectively, and vanishes toward the target edge. There is a qualitative anticorrelation between the distribution of the ion current and the nitrogen areal densities shown in Fig. 1(b). The latter represent stationary distributions after a sufficiently long operation time for each parameter setting. [To achieve the stationary state, the eroded thickness should well exceed the thickness of the nitrided layer. With a sputter yield around 0.4 according to TRIM (Ref. 12) computer simulations, a current density of about 1 mA/cm² corresponds to sputter removal of 2.5 × 10¹⁸ at./cm² s. Thus, with the observed nitrogen areal density of ~1 × 10¹⁵ cm⁻², the stationary state is achieved within about 10 s even at the target center.] The average nitrogen incorporation increases at increasing nitrogen gas...
flow. At the target center, the nitrogen areal density appears to saturate except for the lowest nitrogen flow. When neglecting sputtering, an upper estimate of the saturation areal density can be obtained assuming the formation of stoichiometric TiN within the range of the incident reactive gas ions. The dominant reactive ion species from the discharge is \( \text{N}_2^+ \), which, after acceleration by the target voltage and upon impinging the surface, splits into two atoms of half-energy. The range distribution of the resulting \(~175\) eV N atoms extends to about \(2.7\) nm in Ti, which corresponds to a nitrogen areal density of \(1.5 \times 10^{10}\) cm\(^{-2}\) in rough agreement with the experimental result. Toward the centerline of the racetrack, the nitrogen incorporation decreases by \(~45\)% and \(~10\)% for the lowest and highest nitrogen flows, respectively. The radial position of minimum nitrogen incorporation is in good agreement with that of the maximum current density. Further, toward the edge of the target, the nitrogen areal density increases again in accordance with the decreasing ion flux. However, for the largest nitrogen flows, it increases to a level which is significantly above the saturation level at the target center, although the current density is similar. We ascribe this to some redeposition of Ti and corresponding compound formation in this outer area, although the transport mechanisms of redeposition are not obvious.

As briefly mentioned above, the stationary reactive gas incorporation results from a balance of reactive gas deposition and sputter erosion. The three major mechanisms of reactive gas accumulation are chemisorption of reactive gas molecules at the surface, direct implantation of ionized reactive species, and recoil implantation of the chemisorbed species by ion bombardment. Recoil implantation and sputter erosion are mainly due to inert gas ions, as the nitrogen addition is relatively small and the electron-impact ionization cross sections of \(\text{Ar}^+\) are larger than the ones of \(\text{N}_2^+\). All ion fluxes, and thereby the sputter erosion, follow the radial current distribution of Fig. 1(a), whereas the molecular gas flux arrives uniformly across the target. Thus, if adsorption in connection with recoil implantation plays a significant role for deposition, the deposition-erosion balance is shifted toward erosion in the center of the racetrack compared to the target center and edge, which results in a reduced nitrogen incorporation.

In order to corroborate this picture, quantitative model calculations have been performed. For this purpose, the dynamic global surface model given by Kubart et al., which incorporates the above mechanisms, has been applied to the stationary state. Compound formation at the surface is modeled by chemisorption of incident reactive gas molecules assuming a unity sticking coefficient on the metallic fraction of the surface. The corresponding gas-kinetic fluxes are derived from the nitrogen partial pressure, which has been measured using mass spectrometry for each setting of the reactive gas flow. Of ions, only \(\text{Ar}^+\) and \(\text{N}_2^+\) are taken into account, which are dominant in the discharge according to the electron-impact ionization cross sections. The radially varying total \((\text{Ar}^+\) plus \(\text{N}_2^+)\) ion flux is taken from the radial distribution of Fig. 1(a). (Secondary electron production at the target is neglected, as it is known to be small.) The \(\text{Ar}^+\) to \(\text{N}_2^+\) flux ratio is chosen according to the respective partial pressures and the ratio of the ionization cross sections. The latter is obtained by averaging the cross sections over an energy range extending from the ionization threshold to the target voltage. The yields of surface sputtering and recoil implantation are derived from TRIM (Ref. 12) with \(\text{Ar}^+\) ions incident on 1 ML of TiN on Ti. (The surface binding energies have been chosen according to Ref. 17.) Recoil implantation of surface nitrogen atoms into the bulk and direct implantation of \(\text{N}_2^+\) ions are modeled by a saturable transfer into a fixed monolayer at a depth of \(2.7\) nm (see above). Thus, the model neglects any details of the depth distributions of direct and recoil implantation and any in-depth multiple relocation of the reactive atoms.

Figure 1(c) shows the model prediction of the nitrogen incorporation versus the target radius. At the target center, the experimental results (cf. Fig. 1(b)) are reproduced quantitatively. As discussed above, the discrepancy at the target edge is attributed to redeposition. The sequence of the radial dependencies at different reactive gas flows shows good qualitative agreement between experiment and model results, although the shape of the radial dependencies appears somewhat different with a narrower depression in the racetrack obtained from the model. In particular, for the highest nitrogen flow, the predicted reduction of nitrogen incorporation in the center of the racetrack is in excellent agreement with the experiment. Thus, in view of the simplicity of the model, the agreement between model predictions and experiment can be regarded as being surprisingly good. The inspection of the nitrogen depth profiles obtained from the model shows that the saturated areal density is associated with the formation of a stoichiometric layer, whereas in the nonsaturated region around the racetrack centerline a constant, substoichiometric
ion bombardment in the racetrack not only increases the relative contribution of direct implantation of reactive ions but also transfers chemisorbed nitrogen efficiently to the bulk by recoil implantation, so that a high rate of chemisorption is sustained.

In conclusion, we have demonstrated a significant variation of target poisoning across the target surface during reactive magnetron sputtering of TiN, which depends on the reactive gas admixture. For typical conditions of practical applications with a reactive gas addition of a few percent, the nitrogen incorporation in the racetrack may be reduced by almost 50% compared to the target center and edge. The experimental results are consistent with the simple modeling of the local particle balance. Ion implantation, reactive gas adsorption in combination with recoil implantation, and sputter erosion are confirmed as the main mechanisms of establishing the local target composition in the stationary state.

nitrogen concentration extends from the surface into the depth. In view of the good agreement with the model results, we apply this picture with some confidence also to the interpretation of the experimentally observed areal densities.

In the framework of the above modeling, Fig. 2 illustrates the relative contributions of the mechanisms of nitrogen incorporation at different reactive gas flows and target locations, as calculated for the stationary state. In the present range of reactive gas partial pressure, combined chemisorption and recoil implantation dominates over direct ion implantation. This is consistent with the high gas-kinetic flux of nitrogen molecules relative to the flux of \( N_2^+ \) ions, and an efficient transfer of the chemisorbed nitrogen by recoil implantation into the bulk. At increasing nitrogen partial pressure, the relative contribution of direct ion implantation increases, as the surface becomes increasingly saturated. The latter limits the rate of chemisorption of gas molecules at the surface, and thereby the inward flux by recoil implantation. Comparing the two lines of Fig. 2, the relative contribution of direct ion implantation is somewhat higher in the racetrack. However, the difference is surprisingly small in view of the ion current distribution, which varies by more than one order of magnitude. This is again attributed to the limitation of combined chemisorption and recoil implantation, which occurs preferentially at the target center and edge. The high

![Graph](image-url)

**FIG. 2.** Ratio of nitrogen injection by direct ion implantation and recoil implantation from the surface layer vs the nitrogen partial pressure for different target locations. \( j_{N_2^+} \) and \( j_{N_{\text{recoil}}} \) denote the respective atomic nitrogen fluxes. The partial pressure of 0.07 Pa corresponds to a reactive gas flow of 2.5 SCCM.