Vacuum 89 (2013) 229–232

Contents lists available at SciVerse ScienceDirect

Vacuum

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

Ion beam based composition and texture control of titanium nitride

W. Ensinger [a,*], E. Marin [b], L. Guzman [b]

[a] Darmstadt University of Technology, 64827 Darmstadt, Germany
[b] University of Udine, 33100 Udine, Italy

ARTICLE INFO

Article history:
Received 12 September 2011
Received in revised form
14 May 2012
Accepted 19 May 2012

Keywords:
TiN
Ion beam assisted deposition
Texture

ABSTRACT

Titanium nitride was formed by electron beam evaporation of titanium in an atmosphere of backfilled nitrogen. The growing film was simultaneously irradiated with argon ions. From of a single-aperture ion source, a Gaussian-shaped ion beam was extracted. Each position on the sample was correlated with a particular ion beam current density. With this method, on a single substrate a large variation in ion irradiation intensity could be obtained. Since the titanium evaporation rate was uniform over this area, the parameter varied over the sample surface was only the ion-to-atom arrival ratio. It turns out that with a constant Ti condensation rate and nitrogen impact rate, the Ti:N ratio in the film is a strong function of the argon ion impact rate. Ion-beam induced nitrogen sorption saturates at a certain ion irradiation intensity. While under all conditions the TiN (mono)phase is obtained, it shows different preferred crystal orientations in dependence on ion bombardment intensity. At low level, the film grows in (111)-orientation, at high levels in (100)-orientation. In a small transition zone, (110)-orientation prevails. Thus, the orientation can be selected by the ion beam intensity, which is relevant for application.

1. Introduction

The topic of this paper is Ion Beam Assisted Deposition (IBAD) [1–4] of titanium nitride films. This system has been investigated for decades [5–10] and is one of the most prominent nitride coatings. Others are e.g. silicon nitride [11] and chromium nitride [12–14].

It is well known that energy input into a thin film growing from the vapour phase alters the film's properties, such as its microstructure, chemical and phase composition. This energy input can come from energetic ions. The source of the ions can be a remote ion source [15] or the plasma surrounding the film's substrate [16,17]. The ions are defined by their mass, momentum and kinetic energy. These parameters define the energy per unit area and volume, deposited into the growing film. Apart from physical effects, such as knock-on atom movement and sputtering, chemical influences play a role. This is particularly important, when compound films are deposited, such as oxides and nitrides [1–4]. In case of irradiation of the growing film with an ion source, two techniques can be distinguished: simultaneous irradiation with the compound-forming species, e.g. implantation of nitrogen for forming nitrides, or bombardment with a non-reactive species, typically rare gas ions, in the presence of reactive molecules in the residual gas, such as nitrogen, oxygen, or methane; the latter is also called Reactive Ion Beam Assisted Deposition (RIBAD).

For the present contribution, the latter method was used in a "single shot" technique. Rather than carrying out a large number of experiments with a variation in ion irradiation intensity, one large single sample was used and the parameter to be studied was varied laterally on the sample. This technique has the advantages that much less experimental time is required and that all the parameters to be kept constant are the same, i.e. there are no uncontrolled parameter fluctuations from different experiments. The disadvantage is that the varied parameter is a function of the position on the sample, i.e. there is a parameter gradient, which requires analytical techniques with sufficient lateral resolution.

2. Experimental

The apparatus consists of a cylindrical vacuum chamber with a water-cooled substrate holder on top and an electron beam evaporator and an ion source at the bottom. The ion source has a single aperture with a diameter of 2 mm, emitting an ion beam with Gaussian intensity distribution. The lateral ion current density was measured with a shielded Faraday cup with a 2 mm aperture which was moved through the ion beam perpendicular to it over the sample position. For control, a cellulose sheet was irradiated, and the blackening was measured with a regular optical scanner. The sample was a 4 inch diameter silicon wafer with (100) orientation. Prior to deposition, the chamber was pumped down to

* Corresponding author. Fax: +49 6151 166378.
E-mail address: ensinger@ca.tu-darmstadt.de (W. Ensinger).

0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2012.05.021

a residual gas pressure of 10^{-5} Pa. Electron beam evaporator and ion source were started and operated for a while to reach stable conditions. During that time, both the particle sources and the sample were shielded by shutters. Argon gas was fed into the ion source. This lead to a pressure increase to 10^{-3} Pa. Then, the ion source emission characteristic was measured with the movable Faraday cup. Next, nitrogen gas was backfilled into the chamber up to a pressure of 10^{-2} Pa. Eventually, all shutters were opened and the film was deposited. The deposition rate was measured with a quartz microbalance which was shielded from the ion beam. Ion acceleration voltage was 12 kV, Ti condensation rate was 0.5 nm/s. The process time was 30 min.

After deposition, the wafer was cut in small pieces for analysis. The film phase composition and crystallographic orientation were measured with X-ray diffraction (XRD). The elemental composition was quantitatively measured with Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis for nitrogen (NRA), using the resonant reaction N-15(p, $\alpha\gamma$)C-12 [18,19].

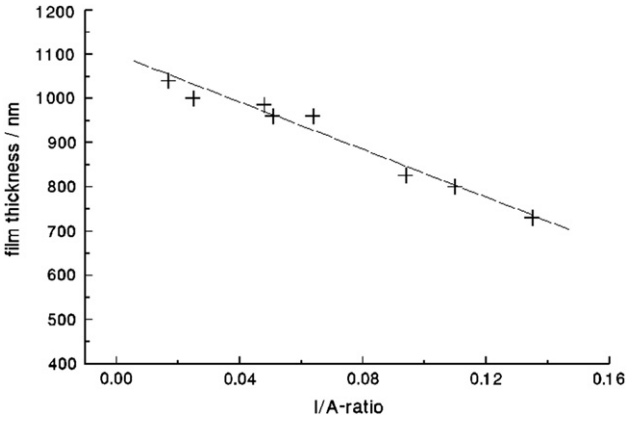

Fig. 2. Thickness of TiN film as a function of I/A-ratio, measured with surface profilometry at an edge.

3. Results and discussion

In the present study, several properties of the TiN film were looked at: the thickness, the amount of nitrogen, incorporated from the residual gas; the amount of implanted argon; the phase composition; the lattice constant and the crystallographic orientation of the grains of the film. These are discussed as a function of the ion-to-atom arrival ratio. The I/A-ratio was calculated from the arrival rate **A** of the Ti atoms from the data of the quartz microbalance. The Ar ion arrival rate **I** was calculated from the ion current density of the shielded Faraday cup. Fig. 1 shows a typical lateral distribution of the Ar ion current density on the substrate. Given a constant Ti deposition rate, the variation of the ion current leads directly to a variation of the I/A-ratio. With a constant nitrogen gas pressure and metal condensation rate, the ratio between condensing Ti atoms and impinging N_2 molecules was also constant. Therefore, the only varied parameter was the I/A-ratio, and it is the influence of this parameter which is the discussion base of this paper.

Before the TiN film properties are discussed, it should be mentioned that under all conditions monophase TiN of the cubic NaCl (B2) structure was found in the XRD. No peaks of metallic Ti or Ti_2N appeared. The width of the TiN phase in the phase diagram is very broad; the system is tolerable to a large range of N in its sublattice [20].

Since the growing film is simultaneously bombarded with a comparatively heavy ion (mass 40 u), there is a certain amount of resputtering observed. A part of the freshly deposited film is lost, leading to a reduced net thickness. This is shown in Fig. 2. The nominal film thickness of 1000 nm, as measured by the thickness monitor, is reduced to 800 nm at an I/A-ratio of 0.11. To first order, the loss in deposited material is a linear function of the I/A-ratio.

An important parameter for phase formation is the nitrogen content of the film. It turns out that Ti under the given conditions incorporates more than 30 at% by the evaporation process itself, without ion irradiation, see Fig. 3. This is due to the very high reactivity of freshly deposited Ti films. For this reason, Ti is being used as pump material in sublimation pumps. The energy gain of the system is high enough to be able to crack the stable N-N triple bond. As soon as the Ar ion beam is switched on, the additional energy delivered to the growing film allows for more nitrogen incorporation. The nitrogen concentration rapidly increases at small I/A-ratios, however it seems to saturate above I/A = 0.08. The benefit of the energy input, leading to an enhanced nitridation, is lost due to sputter decomposition of the nitride film. Another reason is that the phase diagram is well tolerable towards lower than stoichiometric (1:1) composition, but not to excess nitrogen, which can hardly be accommodated in the 1:1 TiN lattice. Fig. 3 shows that the nitrogen saturation limit is close to 50 at%.

In RIBAD, the growing film is irradiated with Ar ions. Following calculation with SRIM [21], the projected range of 12 keV Ar ions in TiN is almost 10 nm. Since the argon ions enter comparatively deep into the film, the question of the whereabouts of argon comes up. This is shown in Fig. 4. It turns out that argon remains in the film to

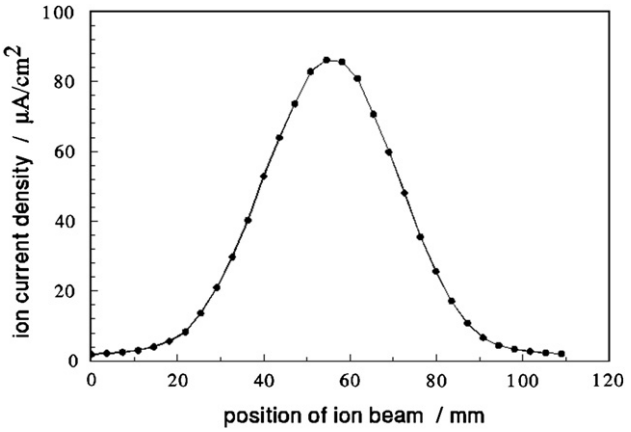

Fig. 1. Lateral distribution of Ar^+ ion current density on the substrate, as measured with a shielded Faraday cup.

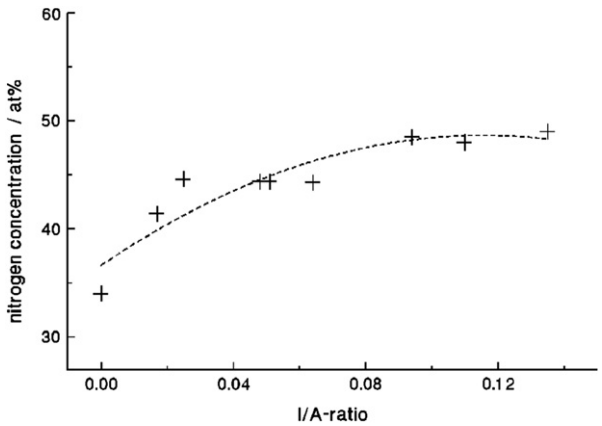

Fig. 3. Nitrogen concentration of TiN film as a function of I/A-ratio, measured with NRA (N) and RBS (Ti, Ar).