PLASMA DEPOSITION OF TiN-LAYERS

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1. INTRODUCTION

In the last five years titaniumnitrid-layers (TiN\textsubscript{x}) have found a wide field of application. In plasma activated physical vapour deposition (plasma-PVD) a nonisothermal plasma with suitable densities of energy and particles causes activation of the components in the volume and on the substrate surface. Chemical reactions in the volume can be neglected relative to those on the substrate surface. By plasma-PVD it is possible to deposit high quality - TiN\textsubscript{x} - layers at temperatures lower than those of the thermodynamical equilibrium.

2. METHOD

TiN\textsubscript{x}-layers have been deposited by hollow cathode arc evaporator (HCAE). The scheme of this equipment is shown in fig.1: a hot hollow cathode (1) produces a highly ionized plasma beam, which will be deflected by a transversal magnetic field (2) to the anode (3).

\textbf{Fig. 1: Basic features of the experiments}
The anode is a water-cooled crucible, which contains evaporating material. Argon flows through the cathode, nitrogen inlet is in the bottom of the bell jar (1). The measurement of plasma-PVD conditions are performed with following methods: LANGMUIR-probes (8), oscillating quartz(9), electron-impact-emission-spectrometer (4)-(6), mass spectrometer (10). TiN$_x$-layers are deposited on substrate (7) with variable bias voltage. The properties of the deposited layers have been measured outside the bell jar.

3. MODEL

A plasma-PVD device can be divided into three parts: particle source - transport space - substrate. The development of a detailed model for the whole system appears to be too difficult. Therefore a simplified scheme was developed to calculate the deposition parameters (2). It comprises three steps:
- measurement of characteristic quantities near the substrate
- calculation from them deposition-relevant parameters
- description of particle transport through the boundary layer from transport space to the substrate and in opposite direction.

A schematic diagram of this model is given in fig.2.

![Diagram showing the calculation of deposition parameters](image-url)

Fig.2: Method to calculate the deposition parameters
4. RESULTS, DISCUSSION

4.1. PLASMAPARAMETERS

Corresponding proposed method (cf. fig.2) the plasmaparameters were measured in the neighbourhood of the substrate. The densities in the transport room of a HCAE are normally so low that free fall regime can be assumed. The form of electron distribution function (EEDF) is very important for plasma description. EEDF is measured by the second derivative of the LANGMUIR-probe characteristic. Examples of EEDF are shown in fig.3 in semilogarithmic representation. The conditions are: 1: \( p_{\text{Ar}} = 0.25 \text{Pa}, \, p_N = 0 \text{Pa}, \, I = 100 \text{A} \); 2: \( p_{\text{Ar}} = 0.25 \text{Pa}, \, p_N = 0.28 \text{Pa}, \, I = 156 \text{A}, \, r_{T1} = 1 \text{mm} \); 3: \( p_{\text{Ar}} = 0.25 \text{Pa}, \, p_N = 0.2 \text{Pa}, \, I = 100 \text{A} \). From fig.3 we can conclude that the assumption of a MAXWELL-EEDF in HCAE is satisfied. The measured electron densities are about \( 5 \times 10^{17} \text{m}^{-3} \).

The measured and calculated temperatures of electrons at variable titanium density/deposition rate \( r_{T1} \) are shown in fig. 4 (1: \( p_{\text{Ar}} = 0.25 \text{Pa}, \, p_N = 0.28 \text{Pa} \); 2: \( p_{\text{Ar}} = 0.78 \text{Pa}, \, p_N = 0.2 \text{Pa} \)). Open circles represent temperatures evaluated from EEDF, filled circles represent temperatures got from static LANGMUIR-probe characteristic. The dotted line show the calculated temperature of electrons in pure titanium. Measured and calculated temperatures show a satisfactory agreement. At chosen

Fig. 3: EEDF in the HCAE. Conditions cf. text

Fig. 4: Comparison of calculated and measured electron temperatures. Conditions cf. text
conditions nitrogen has no remarkable influence on electron temperatures. We start calculation of electron temperature from POISSON-equation, which turns to the plasma balance equation with the assumption of quasineutrality (3). In cylindrical geometry plasma balance equation becomes the following form for a three-component mixture at the boundary plasma-wall:

\[(2kT_e)^{1/2}s_0 = M_1^{1/2}z_1^{1/2}n_1^aR + M_2^{1/2}z_2^{1/2}n_2^aR + M_3^{1/2}z_3^{1/2}n_3^aR\]

with: \(M_\alpha\): mass of ion \(\alpha\), \(z_\alpha^{1/2}\): ionisation rate coefficient (direct ionisation assumed), \(R\): radius of bell jar, \(kT_e\): electron temperature, \(s_0 = \sum_{\alpha} \frac{z_\alpha}{2} (M_\alpha /2kT_e)^{1/2} n_\alpha^a R\), \(n_\alpha^a\): concentration of neutrals.

From plasma balance equation we can calculate the ion portion of components. For a mixture Ar/N\(_2\)/Ti the calculated ion concentration on the axis is shown in fig.5 as a function of titanium deposition rate (\(p_{\text{Ar}} = 0.23\) Pa, \(p_{N_2} = 0.28\) Pa). Ion concentration are related to the electron concentration \(n_\alpha^e\).

**Fig.5:** Ion concentrations, ratio of nitrogen/titanium flux to the substrate, measured stoichiometric factor in a Ar/N\(_2\)/Ti mixture as a function of the deposition rate

At low deposition rate portion of N\(_2^+\) - ions is about 20%.

Dissociative chemisorption of N\(_2^+\)-ions is a very effective process in TiN formation, but at high deposition rate Ar\(^+\)-, N\(_2^+\)-ion portion can be neglected. In fig.5 ratio of nitrogen atoms flux/titanium atoms flux to the substrate is shown at fixed nitrogen pressure \(p_{N_2} = 0.28\) Pa). Arrows show the measured stoichiometric factor \(x\). The measurement of the stoichiometric factor was performed by AUGER-spectroscopy calibrated with standard probes.
4.2. ELECTRICAL PROPERTIES

Electrical properties of TiN$_x$-layers produced by HACE were measured and compared with TiN$_x$-layers produced by sputtering and activated reactive evaporation (ARE). Measured electrical parameters are: specific electrical resistance (SER) (measured by 4-point-method) and temperature stability of the specific contact resistance. These parameters are important by using TiN$_x$ as a diffusion barrier or in electrical contacts. Values of measured SER (\(\phi\)) are shown in Table 1 for HCAE produced and sputtered layers. Composition of the layers was measured by RUTHERFORD-backscattering (RBS) (protons Tab. 1

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>(x)</th>
<th>Rate (\mu)</th>
<th>Phase</th>
<th>(\phi) (\mu)(\Omega)cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCAE</td>
<td>0.54</td>
<td>2.5</td>
<td>(\alpha)-Ti, (\varepsilon)-Ti$_2$N</td>
<td>90 (\pm) 15</td>
</tr>
<tr>
<td>HCAE</td>
<td>0.92</td>
<td>2.5</td>
<td>(\delta)-TiN</td>
<td>28.6 (\pm) 5.6</td>
</tr>
<tr>
<td>Magnetron</td>
<td>0.75</td>
<td>2.5</td>
<td>(\delta)-TiN</td>
<td>180 (\pm) 12</td>
</tr>
<tr>
<td>Magnetron</td>
<td>1.1</td>
<td>0.8</td>
<td>(\delta)-TiN</td>
<td>160 (\pm) 22</td>
</tr>
<tr>
<td>Ti (bulk mat.)</td>
<td></td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>TiN (bulk mat.)</td>
<td></td>
<td></td>
<td></td>
<td>21.7</td>
</tr>
</tbody>
</table>

with 300keV, deflection angle \(\theta=135^\circ\), electrostatic analyzer). Crystallographic structure was studied by X-ray diffraction (Cu, \(K_{\alpha}\), \(K_{\beta}\) radiation) and electron diffraction in a transmission electron microscope (TEM).

SER of TiN$_x$-layers with low N-portion \((x=0.54, \text{HCAE produced})\) shows values higher than those of bulk material (Ti, TiN). TEM and X-ray diffraction show small grained and homogenous microstructure of HCAE produced films.

Fig.6: Contact resistance as function of temperature. Conditions cf. text
without open structures in opposite to sputtered layers. The SER of sputtered layers is about a half magnitude higher.
As diffusion barriers in ohmic contacts on p-GaAs the TiN (x=0.92) layers (HCAE, thickness 25 nm) show high metallurgical stability and prevent strong interdiffusion up to 870 K. This is in accordance with the homogeneity and the dense structure. Examples for the contact resistance (\( R_K \)) as function of temperature are shown in fig.6.

4.3. OPTICAL PROPERTIES

Reflection and transmission measurements were carried out in the spectral range 0.2 - 2.5 \( \mu m \) with \( M \) 40 (Zeiss Jena) and DK-2A (Beckmann) spectral photometers. A MgO-layer in the UV and NIR ranges were taken as reference in reflection measurements. \( \text{TiN}_x \)-layers were prepared on quartz substrates by HCAE with thickness in the range from 10 to 19 nm at constant deposition rate (0.03 nms\(^{-1}\)) and variable \( \text{N}_2 \)-pressure. Thin films of TiN\(_x\) show a transmission window limited by free carrier intraband absorption in the infrared and interband absorption in the ultraviolet range. The maximum of transmission nearly coincides with the minimum of reflection. Both shift to lower energies with increasing nitrogen content (4). This behaviour is shown in fig.7.

Conditions are as following for the nitrogen pressure: 1: 0Pa, 2:0.037Pa, 3:0.064Pa, 4:0.1Pa, 6:0.16Pa, 7:0.19 Pa, 9:0.22Pa, 10:0.2Pa. Curve 1 represents the reflectivity curve of Ti. The TiN\(_x\)-samples show a higher IR reflectivity than films prepared by reactive sputtering. This is in agreement with the higher conductivity of the HCAE-produced layers. The high IR reflectivity of TiN is due to intraband absorption of free carriers and related to conductivity according to the HAGEN-RUBENS relation with \( R=1-4(\tau/\omega_c)(\omega\omega/\lambda)^{1/2} \), where \( \omega \) is SER.

The high optical density of the films is the reason for a
relatively small transmission. Fig. 8 demonstrates the different optical behaviour for different prepared films and for the TiN single crystal (4,5). The plotted imaginary part \( \varepsilon_2 \) of the dielectric function obtained according (6) describes the energy dissipation in the samples. Absorption of HCAE-produced films is higher than those of sputtered films and of single crystal.

Despite differences in the spectral behaviour of the films it is obviously that with increasing nitrogen content the minima in \( \varepsilon_2 \) and \( R \) are

Fig. 8: Imaginary part \( \varepsilon_2 \) of the dielectric function of TiN\(_x\) films prepared by HCAE (curves 3, 4, 10), by high rate sputtering and of the single crystal

shifted to lower photon energies. This can be used for a non-destructive determination of \( x \) in TiN\(_x\). The main features of spectra, however, are similar. The structure at 3.6 eV for the single crystal is missing in the films. Films prepared by sputtering show an electronic structure in reflecting in this energy range when \( x \geq 1 \) (4). Interpretation of the optical spectra on the basis of band structure calculations is not yet permitted, as the dielectric function has not been determined. This is in further consideration.

5. REFERENCES
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