Influences of the nitrogen content on the morphological, chemical and optical properties of pulsed laser deposited silicon nitride thin films


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Abstract

Silicon nitride (SiNₓ) thin films of various stoichiometries (x) were prepared on Si (100) substrates applying the Nd:YAG (λ = 1064 nm) pulsed laser deposition (PLD) process from pure Si targets in the “shaded off-axis” technique at room temperature. The specific arrangement of this technique with perpendicular target and substrate surfaces and a metallic screen in between guarantees very low particulate (droplet) deposition and, thus, excellent surface qualities. The about 80- to 100-nm-thick silicon nitride films have very smooth surfaces (f 0.5–1.5 nm roughness) and dense structures. The N₂ partial pressure strongly influences the nitrogen content and the silicon bonding structure of the films analyzed by means of secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS), resp. As a consequence, the optical properties examined by spectroscopic ellipsometry are tailorable in a wide spectral range between 250 and 1200 nm.

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1. Introduction

Silicon nitride (Si₃N₄) is one of the most interesting thin film materials in the semiconductor and optoelectronic device technology [1,2]. The outstanding advantage of thin films in the silicon–nitrogen system are the tailorable electronic and optical properties, which are highly dependent on the chemical composition. Thus, the deposition of nonstoichiometric silicon nitride (SiNₓ, x < 4/3) desires a precise manipulation of the manufacturing parameters. Furthermore, low temperatures are requested to prevent damage of the devices during film deposition. One of the most suitable techniques combining room temperature deposition with precise manipulation of the deposition parameters is the Pulsed Laser Deposition (PLD) [3–8]. Compared to the CVD techniques, these low deposition temperatures enable the coating of temperature sensitive materials (organic materials, polymers). The PLD is based on a pulsed laser beam evaporating the target material and ionizing the vapor. Besides the ablation of vaporized material also solid and liquid material is ejected from the target, which leads to inadequate surface qualities of the grown films. To overcome this major problem, various proposals have been discussed in the past (e.g. in Ref. [9]). Besides the promising application of excimer lasers, the “shaded off-axis” technique [10–12] seems to be a successful approach, applying a perpendicular arrangement of the target and substrate surfaces combined with a metallic screen to protect the substrate against direct particle flow. Using this technique reduces the deposition rate to about 1/5 to 1/7 of the usually used “on-axis” technique with perpendicular target and substrate surfaces, but scarcely influences the film growth rate compared to the “off-axis” technique without a screen.
The height of the screen was optimised for relatively high deposition rates combined with very low and acceptable droplet densities, detailed in Refs. [11,12].

The aim of the present work was the application of this technique to the reactive PLD of SiN thin films in nitrogen-containing atmospheres for studying the achievable range of film properties. Thus, the chemical and optical properties of the thin films have been investigated by SIMS, XPS and spectroscopic ellipsometry.

2. Experimental

2.1. Film deposition

High purity silicon targets (99.95% Si) were used for the ablation experiments using a pulsed Nd:YAG laser, which provides a beam with 1064 nm wavelength, 0.85 J pulse energy and 10 ns pulse duration at a repetition rate of 10 Hz. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (~25 °C) onto single crystalline (1 0 0) orientated silicon substrates mounted normal to the target behind a screen of 1 cm height (“shaded off-axis” technique), for details see Refs. [11,12]. Prior deposition, the substrates were cleaned ultrasonically in pure acetone and ethanol to remove surface contaminations. The reaction chamber was evacuated before starting the deposition process to pressures below 2 × 10⁻³ Pa by a pumping unit consisting of a rotating pump and an oil diffusion pump. The flows of the process gases (Ar, N₂) (Table 1), which are necessary for the scattering of the ablated species behind the screen to reach the substrate surface, were adjusted by means of electronic mass flow controllers.

2.2. Film characterization

The surface quality of the films was inspected by light microscopy. Atomic force microscopy (AFM) was applied for characterizing the surface structures on a nanometer scale using a Nanoscope III (Digital Instruments) facility. X-ray diffraction (XRD) (Bruker AXS D8 Discover) in grazing angle alignment (0.5° and 1.0°) with CuKα radiation was used for determining the crystal structure of the thin films. The characterization of the chemical film composition occurred by secondary ion mass spectroscopy (SIMS) using a CAMECA IMS 3f [13]. The system has approximately 2 μm lateral and 20 nm vertical resolution. Nearly stoichiometric direct nitrided and hot pressed Si₃N₄ powder was taken as the standard material for quantitative analysis. For measuring the sputter depth in the analyzed area, a mechanical profiler was used.

The determination of the chemical bonding occurred by X-ray photoelectron spectroscopy (XPS) using an Omicron Multiprobe system with a monochromized AlKα (1486.6 eV) X-ray beam and a resolution of the analyzer better than 0.3 eV [14]. The detection sensitivity was approximately 1 mass %. Before taking the spectra, Ar⁺ ion sputtering was applied allowing measurement in the film bulk in about 15–20 nm sputter depth. The quantification of the spectra was performed by using a stoichiometric Si₃N₄ standard material and considering the calibration factors of the XPS facility used. Although the electric charging during the measurement was minded and all spectra were related to the C₁s peak (binding energy ~ 285.0 eV), slight shifts (<0.15 eV) can be present in the XPS spectra.

The optical properties of the films were determined using a variable angle spectroscopic ellipsometer (J.W. Woollam) at incidence angles between 65° and 85° in the spectral range from 360 to 900 nm with 2 nm spectral resolution. For the calculation of the optical constants and the film thickness, the Cauchy dispersion [15] and the Urbach relation [16] were applied in case of the silicon-rich films. In contrast, the fitting of the refractive indices, extinction coefficients and film thickness of the nitrogen-rich films was performed using a graded interface two component model [17] consisting of stoichiometric silicon nitride (Si₃N₄) [18] as top layer and Si-rich silicon nitride [19] as base layer. Due to the higher accuracy of the spectroscopic ellipsometry compared to the SIMS technique, all film thickness given in this work are taken from these measurements.

3. Results and discussion

3.1. Structural and morphological characterization

The surface characterization of the as-deposited thin films in the silicon–nitrogen system, performed by means of light microscopy, revealed nearly particulate-free film surfaces (~ 12,000 cm⁻²). These very clean surfaces are a result of the application of the “shaded off-axis” arrangement of the target and the substrate, preventing a direct hitting of the substrate surface by molten particles (droplets) [10–12]. In general, these droplets are ejected during the interaction of the IR laser beam with the Si target [9]. The film surfaces were found very smooth (surface roughness Rₐ

<table>
<thead>
<tr>
<th>Film sample</th>
<th>Process gas flow (sccm)/gas pressures (Pa)</th>
<th>Film thickness (nm)</th>
<th>Roughness Rₐ (nm)</th>
<th>Binding energy of Si (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>30/1.6</td>
<td>84.1 ± 5</td>
<td>0.51</td>
<td>98.2</td>
</tr>
<tr>
<td>S2</td>
<td>25/1.4</td>
<td>83.6 ± 5</td>
<td>1.05</td>
<td>100.9</td>
</tr>
<tr>
<td>S3</td>
<td>0/30/1.5</td>
<td>96.9 ± 5</td>
<td>1.29</td>
<td>101.3</td>
</tr>
<tr>
<td>S4</td>
<td>0/60/2.5</td>
<td>78.5 ± 5</td>
<td>1.47</td>
<td>103.0</td>
</tr>
</tbody>
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~ 0.5 to 1.5 nm; Table 1). Compared with the initial roughness of the substrate ($R_a = 1.8$ nm, Fig. 1a), a smoothing of the wafer surface by the Si and SiN$_x$ thin films is evident. The lowest values can be observed for the Si film S1 deposited in inert Ar process gas atmosphere (Fig. 1b). The smooth surface, which is free of pores (Fig. 1b), refers to a dense microstructure of this film. The small clusters at the surface are probably caused by growth stresses of the film [20]. By increasing the nitrogen content in the process gas, an increase of the size of some of the cluster and a very flat surface in their surrounding can be observed for low N$_2$ gas flows (S2 in Fig. 1c), while the AFM images of the films S3 and S4 (high N$_2$ gas flow, Fig. 1d–e) present a large number of nanoclusters with an average height of about 1 to 1.5 nm, but indicating a dense microstructure. The increased number of nanoclusters combined with the increased roughness at the higher nitrogen flow seems to be caused by the different chemical composition of the deposits and probably influenced by the plasma composition. As explained afterwards, the chemical binding structure is decisively changed by the addition of nitrogen atoms. The plasma, which is created by collisions of the laser evapo-

Fig. 1. AFM micrographs of the (a) silicon wafer substrate and the PLD films: (b) S1 (gas flow: 30 sccm Ar), (c) S2 (5 sccm N$_2$, 25 sccm Ar), (d) S3 (30 sccm N$_2$) and (e) S4 (60 sccm N$_2$).
rated Si atoms and the process gas atoms, could have effects due to different atomic mass, and/or ionization and kinetic energy of excited species (Ar, N, Si and Si–N atoms and ions). Because of the increase of the roughness of the sample S4, deposited in the higher gas pressure, a low influence seems to be caused by the different deposition gas pressures (Table 1), which decreases the energy of the deposited species at elevated values due to higher scattering.

The XRD investigations using grazing incidence alignment indicate a fully amorphous structure of all films. Similar results were found in TEM investigations of PLD silicon and silicon oxide thin films [11], deposited in “shaded off-axis” arrangement too, and can be attributed to the low energy of the deposited atoms on the sample surfaces during film growth. Although the vaporized target material is partly ionized during the laser ablation, the low energies of the deposited species are characteristic for the PLD technique in the “shaded off-axis” arrangement [10–12], which requires a scattering of the ablated species for reaching the substrate surface. Thus, the surface as well as the bulk diffusion processes, which are necessary for crystal growth in the films, cannot be activated by the low energies during deposition at the low substrate temperatures (∼25 °C).

Furthermore, the scattering of the ablated species decreases the deposition rate. Modeling of spectroscopic ellipsometry data revealed film thicknesses of about 80 to 100 nm after 60 min deposition time. Compared to the deposition with parallel situated target and substrate surfaces (“on-axis” arrangement), these deposition rates in the “shaded off-axis” geometry are about five to seven times smaller.

3.2. Chemical characterization

SIMS and XPS measurements were used to determine the chemical composition of the films. The SIMS depth profiles of the different measured species are shown on the examples of the most different films S1 and S4 in Fig. 2. The latter film is representative for the films S2 and S3 deposited in N₂ containing atmospheres too. All depth profiles indicate contaminations of oxygen, carbon and hydrogen atoms and increasing concentrations near the native oxide layer covering the silicon wafer. Comparing the element count rates of O and H of the N-rich film S4 (Fig. 2b) and the nearly N-free film S1 (Fig. 2a), an about 10 times lower O contamination is present in the latter film, which can be attributed to differences in the plasma formation and reaction mechanisms in the different gas atmospheres. The count rate for the nitrogen containing species Fig. 2. SIMS depth profiles of the PLD films (a) S1 and (b) S4, deposited in atmospheres of 30 sccm Ar and 60 sccm N₂, resp. The measured counts of SiN and CN ions and O, H and C contaminations are related to 10⁵ counts of Si ions.

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Fig. 3. (a) Dependency of the nitrogen content on the sputter depth of the PLD films obtained by quantified SIMS depth profiles and stoichiometric Si₃N₄ as standard material. (b) Average nitrogen contents in the films in dependency of the nitrogen gas flow during deposition.
detected (SiN, CN) in all films deposited in N₂ containing atmospheres (e.g. S₄ in Fig. 2b) is nearly constant over the whole film thickness. The carbon and hydrogen atoms contaminating the films originate from the oil diffusion pump used for evacuating the recipient. The XPS results, shown in Fig. 4a, reveal the presence of O, C and Ar atoms too. Quantified depth profiles of the N contents calculated using a stoichiometric Si₃N₄ standard are shown in Fig. 3a. The small fluctuations in the elemental concentration are caused by the SIMS equipment used. The results, shown in Fig. 3b as average values and deviations over the film thickness (film surface to native oxide layer on the substrate), indicate the increase of the nitrogen content at higher N₂ gas flows during deposition.

The increase of the nitrogen content was also found in the XPS investigations of the silicon peaks (Fig. 4b). The binding energy of the silicon atoms is shifted from 98.2 eV in the film S₁, which is the near the characteristic value of 98.6–99.2 eV for the metallic bonding (Si⁰) of the Si atoms [21,22], to 100.9 and 101.3 eV for the films S₂ and S₃, resp. The binding energy of 100.9 eV can be attributed to chemical bonds of a central Si atom with two Si and two N atoms in its surrounding [23], resulting in an Si²⁺ or Si₃N₂ structure. Small contents of Si₃N₄ type bonds (Si⁴⁺) are indicated by the nonsymmetrical shape of the Si XPS peaks. A quantification of the nitrogen contents of the films S₂ and S₃ from the XPS analysis results in about 46.8 and 52.4 at.% N. These findings corresponds well to the SIMS results (Fig. 3b). Fully Si₃N₄ type bonding, characterized by the Si⁴⁺ state with a binding energy of about 103.2 eV [22,23] dominate the chemical structure of the N-rich film S₄ (binding energy ~ 103.0 eV) with a quantified N content of 56.6 at.%. The detailed spectra of N peak showed a slight shift from the pure Si–N bonding to partly N–N type bonding (Fig. 4c), leading to high contents of nitrogen too. For the N atoms, binding energies of about 397.5 eV are found for the films S₂ and S₃ deposited atmosphere of lower N₂ partial pressure, indicating the N₃⁻ state of the N atoms and, thus, three saturated bonding sites for Si atoms [24] (Fig. 4c).

3.3. Optical characterization

The differences in the chemical composition and bonding crucially influence the optical behaviour of the films. The dependencies of the refractive indices as well as the extinction coefficients on the wavelengths between 260 and 900...
nm are shown in Fig. 5a and b, resp. For the nearly pure Si thin film S1, the optical behaviour can be described excellenty by amorphous Si (a-Si) [18]. For the films with high N contents (S3, S4), the optical constants fit well with data of noncrystalline, stoichiometric Si3N4 [18]. The optical behaviour of the film S2 represents a transition between a-Si and Si3N4, like the Si-rich Si3N4 labeled functions [19].

These results verify the varying bonding structure of the Si atoms in amorphous Si–N networks found in the XPS investigations. Si–Si bonds are replaced by Si–N bonds at higher N contents of the films. Reasonably, the bonding of the Si atoms changes from the metallic Si0 structure to Si+, Si2+ and Si3+ at higher N concentrations and finally, reaching the saturation of the four possible bonding sites of the Si atoms by four N atoms, to Si4+.

The N atoms possess independently on the N content in the films S2, S3 and S4 deposited in N2 atmosphere three binding sites (N3– structure), which are all bonded to Si atoms in their surrounding. These results confirm a network of Si and N and S4 deposited in N2 atmosphere three binding sites (N3–, S2, S3 and S4) deposited in N2, where at higher N contents the films S2, S3 and S4 deposited in N2 atmosphere three binding sites (N3– structure), which are all bonded to Si atoms in their surrounding. These results confirm a network of Si and N atoms with lower order only on the atomic scale described by Karcher et al. [23] for nonstoichiometric SiN4, (x ≠ 4/3) films.

4. Conclusions

The Pulsed Laser Deposition (PLD) technique with an Nd:YAG laser (1064 nm wavelength) was applied for manufacturing thin films in the silicon–nitrogen system from silicon targets at room temperature. By varying the Ar/N2 gas flow ratio in the reactive deposition process, the nitrogen content of the growing thin films was influenced. The application of the “shaded off-axis” PLD technique with a perpendicular arrangement of the target and the substrate surfaces and a screen in between for preventing a direct deposition without scattering leads to nearly particulate (droplet) free films with very smooth surfaces and dense structures. The necessity of scattering decreased the energy of the vaporized atoms and clusters deposited and, thus, lead to fully amorphous film structures. These collisions between the Si atoms and N2 molecules cause chemical reactions, which are mainly responsible for the chemical composition of the films, found between nearly pure Si for the deposition in Ar atmosphere and Si3N4 in N2 containing atmospheres. The optical behaviour (refractive indices, extinction coefficients) of these films is comparable with amorphous silicon and stoichiometric Si3N4 found in literature, whereas the film with a lack of nitrogen shows a transition-like behaviour between these two compounds. This phenomenon confirms the bonding structure in the amorphous film structure found in the XPS investigations. In dependency of the N content of the thin films, the amount of Si–N bonds in the amorphous network varies and the bonding type of the Si atoms changes between Si+, Si0, Si2+, Si3+ and Si4+ with increasing N content. In contrast, the nitrogen atoms are independently N3– bonded with Si atoms in their surrounding.

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References