Applied Surface Science 282 (2013) 226–230

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Influence of oxygen pressure and substrate temperature on the properties of aluminum fluoride thin films

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ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form 23 May 2013
Accepted 23 May 2013
Available online 30 May 2013

Keywords:
Aluminum fluoride
Optical constants
Laser-induced damage threshold

ABSTRACT

Single layers of AlF_3 were deposited at different substrate temperature by resistant heating technique in vacuum and in certain oxygen pressure. The chemical composition, total stress, optical constants and laser damage resistance were characterized. Comparative study indicates that AlF_3 films deposited under certain oxygen pressure and lower temperature tend to absorb more water when exposed to air and as a result, their total stress and optical absorption are reduced. These differences and the increased laser-induced damage threshold (LIDT) at 355 nm demonstrate that reasonable oxygen pressure and substrate temperature may improve AlF_3 films' UV performance.

1. Introduction

With the wide spread application of UV/DUV-excimer lasers, the requirement for optical thin film components with low absorption losses and high laser damage resistance has always been increasing [1]. Optical materials normally have higher optical absorption with decreasing wavelength, so materials with larger energy band gap are preferred. Researches have revealed that the fluorides have generally lower extinction coefficients than the oxides [2]. Damage test results also indicate that fluoride coatings have higher laser-induced damage threshold (LIDT) than commonly used oxide coatings [3–5]. Fluoride materials are promising candidates for UV/DUV coatings, but absorption by defects and the high tensile stress are the major limitations in their wide spread application.

The properties of optical coatings are strongly influenced by their deposition parameters. Previous work has illustrated the relationship between deposition parameters and properties of LaF_3 and MgF_2 monolayers [6–10]. These results, along with the research on ion-beam-assisted LaF_3 and MgF_2 thin films [11–13] have motivated us to conduct a close research on another UV optical material, AlF_3. Our work has revealed that the formation of oxides in AlF_3 thin films may reduce optical absorption and increase refractive index of AlF_3 films [14]. In order to further investigate such effects, AlF_3 thin films were prepared under certain oxygen pressure, and the properties of those samples were characterized and compared with those prepared in vacuum.

2. Experiments

2.1. Sample preparation

AlF_3 thin films with thickness of about 300 nm were prepared on super-polished fused silica substrates by resistant heating in a Leybold SyrusPro 1110 DUV coater equiped with a Mo boat. A vacuum system containing a cryopump and a Meissner trap was engaged to reach the starting pressure of 2.7×10^{-4} Pa. All the substrates were HF etched before a supersonic cleaning process was conducted to eliminate the influence of subsurface defects [15,16]. The cleaning and coating processes were operated in a clean room with dust density of 1000–10000 ft^{-3}. The substrate temperature and coating pressure are described in Table 1. In sample B1 and B2, high purity oxygen was injected into the coating chamber to maintain the required pressure.

2.2. Sample characterizations

A Thermal Scientific Kα X-ray Photoelectron Spectrometer was utilized to measure the chemical composition and bonding energy of the samples.

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http://dx.doi.org/10.1016/j.apsusc.2013.05.108

Table 1
Substrate temperature and coating pressure of samples prepared in high vacuum (A1, A2) and in oxygen (B1, B2).

Group	Substrate temperature (K)	Coating pressure (Pa)
A1	473	2.7×10^{-4}
A2	573	2.7×10^{-4}
B1	473	2×10^{-2}
B2	573	2×10^{-2}

The stress of films was obtained using curvature measurements. The total stress (σ_{tot}) of thin film can be calculated from Stoney's equation [17]:

$$\sigma_{\text{tot}} = \frac{E_S}{6(1-\nu_S)}\frac{t_S^2}{t_f}\left(\frac{1}{R_2}-\frac{1}{R_1}\right) \qquad (1)$$

where E_s and ν_s refers to the Young's modulus and Poisson ratio, while t_s and t_f represent the thickness of substrate and film, and R_1 and R_2 is the radii of substrate before and after deposition, respectively. The change in $1/R$ could be calculated from the change in power, which could be measured from a Zygo MarkIII-GPI Digital Interferometer.

A Perkin-Elmer Lambda 1050 UV/VIS/NIR spectrometer was employed to measure the transmittance and reflectance spectra of each sample. The refractive indices (n) of the films were calculated by envelop method [18] with optical design software (Essential Macleod). The Extinctive coefficient (k) was obtained following the equation [19]:

$$k = \left(\frac{\lambda}{4\pi d}\right)\ln\left(\frac{1-R}{T}\right) \qquad (2)$$

where R and T stand for the transmittance and reflectance, λ for the wavelength, and d for the thickness of AlF_3 film.

The LIDT measurement was performed in the "1-on-1"mode following ISO standard 21254-1 on a set up described in Ref. [7]. A tripled Nd:YAG laser system with wavelength of 355 nm, pulse width of 8 ns and Gaussian radii of 240/320 μm was engaged as the illumination source.

3. Results and discussions

3.1. XPS results and discussion

The major composition of AlF_3 film are F, Al, O and C. The oxygen injection in the coating process leads to considerable increase in the content of oxygen in the thin films, which exists mainly in two forms, water, which was absorbed into the porous structure in atmosphere, and alumina, which was considered to be the result of the formation of Al—O band.

To figure out the composite that contains oxygen, high-resolution XPS spectra of Al2p (Fig. 1) and O1s (Fig. 2) were surveyed at 50 nm etching depth. Asymmetric XPS curves were observed in both O1s and Al2p spectra, indicating the split of oxygen and aluminum peaks, which are evidences for the formation of oxides in the films.

The emergence of aluminum dioxide has resulted in the split of Al2p peaks into two peaks including the Al—F bond peak near 77.7 eV and the Al—O peak near 76.2 eV (Fig. 1). In the O1s spectra (Fig. 2), the higher peaks at around 532.5 eV are due to the O—H bond (absorbed water), while peaks at about 531.5 eV result from O—Al bond. The content of oxygen from water and alumina are calculated and depicted on Fig. 3. In general, samples in group B contain more oxygen than group A, indicating that higher oxygen backfill pressure contributes to water absorption. On the other hand, samples prepared at 473 K (A1, B1) contain more water than those deposited at higher temperature (A2, B2). The difference in water content could be explained by the formation of more porous structures in high pressure and at low substrate temperature, as was observed in MgF_2 films [10].

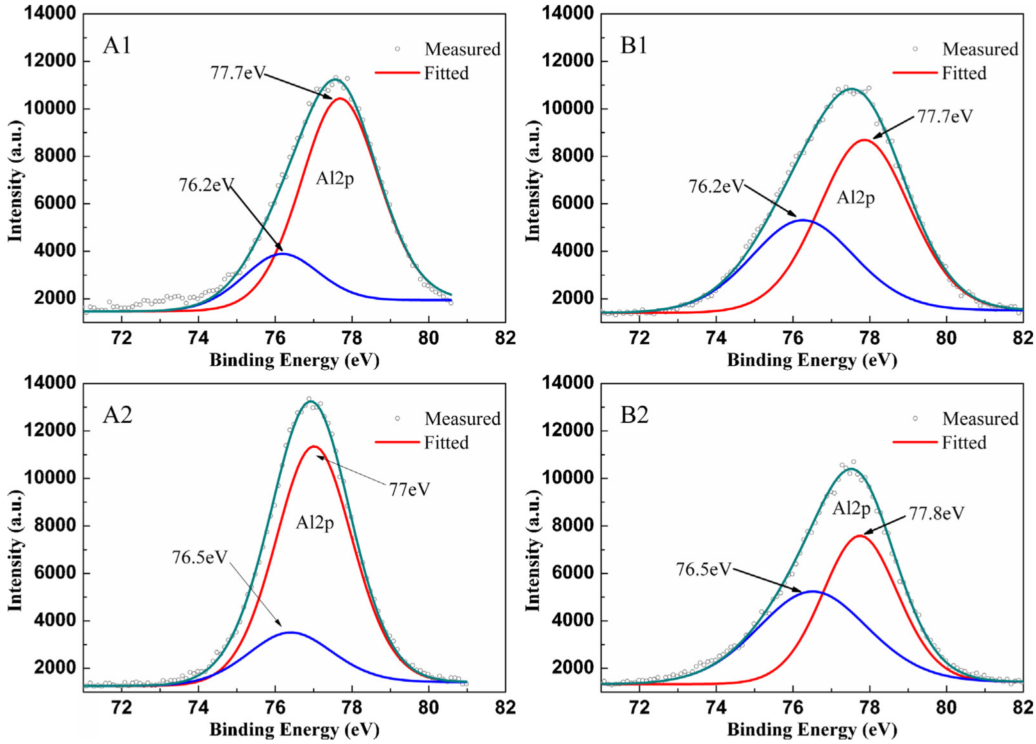

Fig. 1. High-resolution XPS spectra of Al2p for sample (A1) 473 K. (B1) 473 K with oxygen, (A2) 573 K, and (B2) 573 K with oxygen.