OPTICAL PROPERTIES DEPENDENCE WITH GAS PRESSURE IN AlN FILMS DEPOSITED BY PULSED LASER ABLATION

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Abstract. AlN films were deposited by pulsed laser deposition technique (PLD) using an Nd: YAG laser (λ = 1064 nm). The films were deposited in a nitrogen atmosphere as working gas; the target was an aluminum high purity (99.99%). The films were deposited with a laser fluence of 7 J/cm² for 10 minutes on silicon (100) substrates. The substrate temperature was 300 °C and the working pressure was varied from 3 mtorr to 11 mtorr. The thickness measured by profilometer was 150 nm for all films. The crystallinity was observed via XRD pattern, the morphology and composition of the films were studied using scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis (EDX), respectively. The optical reflectance spectra and color coordinates of the films were obtained by optical spectral reflectometry technique in the range of 400 cm⁻¹- 900 cm⁻¹ by an Ocean Optics 2000 spectrophotometer. In this work, a clear dependence of the reflectance, dominant wavelength and color purity was found in terms of the applied pressure to the AlN films. A reduction in reflectance of about 55% when the pressure was increased from 3 mtorr to 11 mtorr was observed. This paper deals with the formation of AlN thin films as promising materials for the integration of SAW devices on Si substrates due to their good piezoelectric properties and the possibility of deposition at low temperature compatible with the manufacturing of Si integrated circuits.

1. Introduction
Aluminum nitride (AlN) possessing a wide band gap of 6.3 eV is a promising dielectric material. For instance, it can serve as the gate dielectric in high voltage and high power electronic devices. AlN is also being investigated as a substitute for the silicon dioxide buried layer in silicon-on-insulator (SOI) substrates due to its low thermal expansion coefficient, high breakdown dielectric strength, and high chemical and thermal stability [1]. Furthermore the metal nitrides based on AlN films, presents high interest because of their electrical, optical and acoustical properties [2]. Their hardness and thermal coefficients of expansion are comparable to that of Si. AlN is used for acoustic wave devices on Si, optical coatings for spacecraft components, heat-sinks in electronic packaging applications, as well as electroluminescent devices in the wavelength range from 215 nm to the blue end of the optical spectrum [2]. Some optical properties near the fundamental band gap of AlN have been reported by Yamashita et al. [3] since 1979. Several theoretical studies have been performed [4, 5], but reliable experimental data [2] have been reported only recently, because both the sample quality and

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spectroscopic techniques have been improved substantially in recent years. Precise knowledge of the optical constants is particularly important in view of the use of AlN thin films in optical filters and light emitting laser diodes, because they show also temperature dependence [6]. Pulsed laser deposition (PLD) is largely applied for processing thin films and other structures. The highly nonequilibrium nature of the PLD process is attractive for the synthesis of stoichiometric thin films of various metal nitrides, carbon nitrides, oxides and oxido-nitrides from the corresponding bulk targets. PLD appears to be a suitable method to transfer stoichiometrically complex single layer structures from AlN ceramic structures to substrates. Many IR measurements presented in the literature were used to estimate the film quality. The spectra provided important information about the composition, homogeneity, crystallinity and the residual stresses present in the films. Moreover, the ellipsometric and reflectance measurements have been used to determine the refractive index in many AlN compounds. Because the ellipsometry and reflectance are a sensitive and non-destructive techniques used for studies of optical properties and microstructures of surfaces and thin films [2]. On the other hand single-chip front-end RF modules incorporating surface acoustic wave (SAW) filters are a matter of intense research. At present these modules are fabricated by bonding single crystal piezoelectric SAW devices onto integrated circuits. Thin films of polycrystalline aluminum nitride (AlN) are promising materials for the integration of SAW devices on Si substrates due to their good piezoelectric properties and the possibility of deposition at low temperature compatible with the manufacturing of Si integrated circuits. AlN thin films of sufficient quality for SAW applications can be obtained by the PLD technique [7]. The goal of this work is to study the effect of the applied deposition pressure on the structural, chemical, morphological and optical properties of binary AlN films deposited by PLD on Si (100) for use in optical applications. We report herewith new results in depositing AlN films from Al targets with N as working gas and their characterization by glancing incidence (GIXRD), X-ray photoelectron spectroscopy (XPS), along with reflectance investigations, and scanning electron microscopy.

2. Experimental Details

The experiments have made in usual PLD configuration consisting of a laser system, a multi-port stainless steel vacuum chamber equipped with a gas inlet, a rotating target and a heated substrate holder. An Nd:YAG laser that provides pulses at the wavelength of 1064 nm with 9 ns pulse duration and repetition rate 10 Hz was used. The laser beam was focused with an \( f = 23 \) cm glass lens on the target at the angle of 45°, with respect to the normal. The target rotated to 2.2 rpm to avoid fast drilling. The distance between the target and the substrate was 6.5 cm. Before deposition the vacuum chamber was evacuated down to 1\( \times 10^{-5} \) mbar by using a turbo-molecular pump backed with a rotary pump. The films were deposited in nitrogen atmosphere as working gas, and aluminum target (99.99%) as metal source. The Films were deposited with a laser fluence of 7 J/cm² for 10 minutes on silicon (100) substrates. The temperature substrate was 300 °C and the working pressure was varied from 3 mtorr to 11 mtorr. The thickness of the films measured with a profilometer was 150 nm for all films. For all the films the deposition time was 10 min.

The crystallinity was observed via XRD pattern by using a Philips-MRD diffractometer. An exhaustive X-ray photoelectron spectroscopy (XPS) study was carried out for AlN films. So, XPS was used on AlN samples to determine the chemical composition and the bonding of aluminum and nitrogen atoms using ESCA-PHI 5500 monochromatic Al Kα radiation and a passing energy of 0.1 eV. The surface sensitivity of this technique is so high that any contamination can produce deviations from the real chemical composition, therefore, the XPS analysis are typically performed under ultra high vacuum conditions with a sputter cleaning source to remove any undesired contaminants. Optical reflectance spectra and color coordinates of the samples were obtained by spectral reflectometry in the range 400 cm⁻¹ – 900 cm⁻¹ by means of an Ocean Optics 2000 spectrophotometer. The coated samples received the white light from a halogen lamp illuminator through a bundle of six optical fibers, and the light reflected on the samples was collected by a single optical fiber and analyzed in the spectrophotometer. The fiber was fixed in perpendicular position to
the sample surface. An aluminum mirror film freshly deposited by rapid thermal evaporation in high vacuum was used as the reference sample, and the experimental spectra were normalized to 100% reflectance of the reference sample. The morphology and micro-device structure on AlN surface films was analyzed by scanning electron microscopy (SEM) (Leika 360 Cambridge Instruments).

3. Results and discussion

3.1. GIXRD Results

Some measures to minimize this effect can be taken for highly monocrystalline-texturized substrates, like silicon wafers, such as dephas ing the angles for the x-ray source and the detector for a given $\Delta \theta$ (usually around 0.5-1º). This has been employed in most of the Bragg-Brentano measurements and diffractograms shown in this AlN results done in a Philips-MRD diffractometer. A different configuration, more appropriated in such cases of highly oriented, ultra-thin or light material-based coatings, is the “Glancing Incidence” or C configuration, where the angle between the sample and the x-ray source is always low ($\omega$ below 5º) and fixed, while the detector undergo an scanning move in $\theta$ with regular steps. The simple equation that rules the observation of an X-ray diffraction peak signal at GIXRD configuration is:

$$\omega + \psi = \theta$$

stating that $\omega$ (angle of incident x-ray beam to surface) plus $\psi$ (angle of a family of planes with the surface) has to be equal to $\theta$ (angle of diffraction related to the interplanar distance of the same family of planes).

In this GIXRD results (Fig.1) is possible to observe the AlN film, which exhibit a crystal structure with crystallites oriented at differents Bragg planes. In this particular case the AlN film show a high texture with preferential (hexagonal) orientation (0002) [8], furthermore, was observed others crystallites that present diffraction consequent to cubic structure in the Bragg planes (111) and (200) [9].

On the other hand, is possible to observe below the preferential orientation associated to Si (100) substrate, which is not observed in this crystallographic pattern (GIXRD), therefore, all Bragg planes are in relation only to AlN films refraction.

![Figure 1](image-url)  

**Figure 1.** XRD pattern for AlN films deposited to 300 °C and 7 mtorr. Dash lines indicate the position of the peaks obtained by JCPDF files from ICCD cards.
3.2. XPS Results

The high-resolution spectra of Al2p, and N1s, were recorded from AlN films, as shown in Fig. 2. From Fig. 2(a), the Al2p peak is composed of a shoulder separated by 1.7 eV with intense peak. The XPS spectrum of Al2p can be fitted well by two Gaussian functions. The values of binding energies obtained for the Al2p peak was 73.9 eV and the higher value for Al2p was 75.9 eV, respectively. According to the literature [10-12] for the Al2p peak, the first one (73.9 eV) and the second one (75.9 eV) can be assigned to Al–N and Al O bonds. The appearance of the peak at 73.9 eV clearly shows that Al has reacted with N; therefore, it can be assigned to Al N [11, 12].

Fig. 2(b) N1s peak is composed of spin doublets, each separated by 2.9 eV. The XPS spectrum of N1s can be fitted well by two Gaussian functions depicts the N1s spectrum with values at, 397.3, and 400.2 eV characteristic for N-N and Al-N bonds, respectively [13, 14]. The XPS results demonstrate that Al atoms bonded to N in the form of nitride, because the elemental concentration of the Al N film was obtained by adjusting the laser incidence on Al target, and the N2 as working gas. In this research, it was discovered that amounts of Al(N) in the Al N film were maximum in the current establishment of process conditions and the ratio of Al and N in the film was about for 2:1. Generally, formative Al(N) phase indicates that the aluminum and nitrogen activity and activation energy provided by the present deposition conditions are enough for the formation of a Al N thin film. Although the surface temperature of the substrate during deposition of Al N film is around 300 °C, the substrate lies in a high-density plasma region and a high ion-to-atom ratio of aluminum and nitrogen can be propitious to the formation of Al N phase at the low temperature below 330 °C. Therefore, calculation of the peak areas without O1s contribution gives an atomic ratio of Al:N = 0.392 : 0.588, which is similar to the stoichiometry of Al0.40N0.60 [15].

![Figure 2. High-resolution XPS spectrum of: (a) Al2p and (b) N1s from Al-N film.](image)

| Atomic composition (at.%)          |
|------------------------------------|
| Al-N films                         |
| **Substrate** | **Pressure (mtorr)** | **Al** | **N** | **O** |
| 300 °C     | 7                  | 39.2   | 58.8  | 2.0    |

3.3. Dominant wavelength and color purity analysis

The reflectivity measure is the fractional amplitude of the reflected electromagnetic field, while reflectance refers to the fraction of incident electromagnetic power that is reflected at an interface. The reflectance is thus the square of the magnitude of the reflectivity. The reflectivity can be expressed as
a complex number as determined by the Fresnel equations for a single layer, whereas the reflectance is always a positive real number.

In certain fields, reflectivity is distinguished from reflectance by the fact that reflectivity is a value that applies to thick reflecting objects. When reflection occurs from thin layers of material, internal reflection effects can cause the reflectance to vary with surface thickness. Reflectivity is the limit value of reflectance as the surface becomes thick; it is the intrinsic reflectance of the surface, hence irrespective of other parameters such as the reflectance of the rear surface. On the other hand, the dominant wavelength (of a colour stimulus) is defined as: “the wavelength of the monochromatic stimulus that, when additively mixed in suitable proportions with the specified achromatic stimulus, matches the colour stimulus considered” [16].

In this work the AlN films has been compared with pure aluminum because the aluminum mirror finish has the highest reflectance of any metal in the 200 nm–500 nm and the 3000 nm–10000 nm (far IR) regions, while in the 500 nm–700 nm visible range it is slightly outdone by AlN and silver, but in the 700 nm–3000 nm range (near IR) it is slightly outdone by, gold, and copper materials [17]. Fig. 3 shows the optical reflectance spectra of the AlN single layers obtained at different deposition pressures. The reflectance of the aluminum and the eye sensitivity are shown for comparison. The spectra of the samples show high reflectances for long wavelengths, near to 62% for the AlN films deposited with 3 mtorr and close to 28% for AlN films deposited with 11 mtorr. These values of reflectances at these wavenumbers agree well with previous reports in the literature for AlN films. A clear decrease in reflectivity for short wavelengths is seen, characteristic of a system with high free-electron density with a reflectance edge below 530 nm due to a screened plasma resonance [18]. The white and aluminum colors of the AlN films are a result of the steep plasma reflection edge that occurs in the visible region where the reflectivity minimum is around 540 nm.

The color purity changes with the deposition temperature, in this study ranges from 0.62 to 0.71 for AlN films, away from the color purity of pure aluminum (0.90), confirming that the films are less white compared with the aluminum. Color coordinates of AlN single layer films are shown in Fig. 3b. Reference coordinates of pure aluminum are shown for comparison. The results of color measurement indicate that all films reflect a hue slightly shifted far to the white as compared to aluminum reflectivity and with similar color purity.

**Figure 3.** Dominant wavelength and color purity results: (a) Optical reflectances of AlN films deposited onto Si (100) substrates at different deposition pressure, also aluminum optical reflectances and eye sensibility were also plotted as references. (b) Chromatic diagram, in the x, y coordinates, of the reflectivity for AlN films. White coordinates of achromatic point are located at (1/3, 1/3).
In this work high dependency on reflectance percentages was also found when the deposition pressure is varied from 3 mtorr to 11 mtorr, therefore, the changes in optical properties can be related not only with changes on temperature deposition but also with generated on morphology surface films due to variation of deposition pressure (Fig 4a.). The Fig. 4a exhibit one constant region for wavelength into of 760 nm-800 nm, in those regions is possible appreciates the effect deposition pressure on reflectance of the films. Fig 4b. Show the decreasing of reflectance when temperature is increased, which indicate that pressure also promotes the absorbance in the AlN deposited via PLD.

From the reflectance spectra it is seen a weak but clear effect of deposition pressure on the optical properties. As the pressure is decreased, the reflectance of the films tends to be higher in the near infrared region, while the minimum in reflectance, between 562 nm and 571 nm for all the films. Dominant wavelength and color purity have been calculated from the reflectance spectra of all films (Table 2). The dominant wavelength was varied for all the samples, from 562 nm ~ 570 nm. AlN films deposited with lower pressure are situated little close to that of pure aluminum reference (574 nm).

| Deposition pressure (mtorr) | Dominant wavelength (nm) | Color purity | Axis X | Axis Y |
|----------------------------|--------------------------|--------------|--------|--------|
| 3                          | 571                      | 0.71         | 0.329  | 0.341  |
| 4                          | 570                      | 0.66         | 0.343  | 0.362  |
| 7                          | 567                      | 0.63         | 0.242  | 0.123  |
| 11                         | 562                      | 0.62         | 0.210  | 0.119  |
| Reference                  | Aluminum                 |              |        |        |
|                            |                          | 574          | 0.90   | 0.358  | 0.371  |

In the Fig. 5a it can be observed the influence of deposition pressure on color purity. This graph shows the increase of purity values towards color gray purity. In the Fig. 5b are observed the differences in the dominant wavelength for all AlN films deposited with different deposition pressures. The
wavelength is an important optical characteristic for different materials. So, when the wavelength is changed is possible observe that natural color is changed. The purity color dependence in AlN films with pressure obtained in this work demonstrates the possibility of some purity color control.

![Graph showing color purity and dominant wavelength vs deposition pressure](image)

**Figure 5.** Color results for AlN films deposited with 7 mtorr: (a) color purity as function of deposition pressure and (b) dominant wavelength as function of deposition pressure.

### 3.4. Scanning electron microscopy analysis

SEM was carried out to quantitatively study the surface morphology of our samples in relation to an increase on deposition pressure in AlN films grown onto Si (100). Fig. 6 shows SEM micrographs for AlN films with random distribution of micro-particles or micro-drops that was analyzed on these surfaces. Therefore, the deposition pressure affects clearly the increase of micro-drops; this can be possible due to low surface mobility when the pressure was varied from 3 mtorr to 11 mtorr. This surface mobility reduces the possibility that the micro-drops are anchored on the surface when arrives with high energy on AlN film. Other possible reason can be associated with the mean free path that produces surface diffusion of nano-drops or micro-drops which can decrease the overall number of particles.

![SEM micrographs](image)

**Figure 6.** SEM micrographs where is observed the micro-particles or micro-drops: (a) AlN films deposited with 3 mtorr (b) AlN films deposited with 11 mtorr.
A molybdenum (Mo) layer of 0.4 μm thicknesses was applied to the deposited AlN samples by the electron beam vacuum evaporation technique. A photolithographic method was used for etching. It was successfully defined an interdigital structure, with lines 7 μm wide, 200 μm long, separated from each other by 7 μm. A typical image is given in Fig. 7a. The magnification image showed in Fig. 7b exhibit that Mo lines are continuous, without any interruption or short-circuit. After the electrical measurements, was possible deduced an insulator behavior for our AlN structures, a good prerequisite for using them as surface acoustic wave (SAW) devices.

Figure 7. SEM micrographs showing the interdigital structure of Mo coating on AlN films obtained by PLD: (a) general interdigital structure, (b) magnification images where is possible to observe the wide and distribution lines that conform the interdigital device.

4. Conclusion
AlN films were grown on Si (100) substrates by PLD using an Al target in N₂ as working gas. The deposition pressure was varied from 3 mtorr to 11 mtorr to analyze their effect upon films optical and morphological properties. The XRD result exhibited the hexagonal (0002) phase. X-ray photoelectron spectroscopy (XPS) confirmed the formation of the binary films. The study revealed that pressure deposition has a marked influence on the physical nature of all the films. It was found a decreasing in the reflectance of 55%, a reduction of color purity about 13% and decreasing in the dominant wavelength around 1.6% with deposition pressure between 3 mtorr and 11 mtorr. Furthermore in this work was evidenced that the deposition pressure affects clearly the reduction of micro-drops; this can be possible due to great surface mobility by the mean free path when the pressure was varied from 3 mtorr to 11 mtorr. Finally was possible to design an interdigital structure with Mo circuit on AlN films like an insulator, which can be used as surface acoustic wave (SAW) devices.

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