Effect of incident laser fluence on the structure of pulsed-laser deposited AlN films

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Polycrystalline AlN films were synthesized on (100)Si substrates by pulsed laser deposition at 800°C and different incident laser fluences and nitrogen ambient pressures. We used two KrF* (λ= 248 nm) excimer laser sources generating pulses of 7.4 and 25 ns duration, respectively. The incident laser intensity was kept constant in all experiments within the range (3 – 4) x 10^8 W/cm^2. The effect of incident laser fluence on the structure and defects of pulsed laser deposited AlN films was investigated by X-Ray diffractometry and frequency-dependent admittance measurements at zero DC bias voltage. The X-ray diffraction results revealed a polycrystalline structure with predominantly cubic crystallites in films deposited with short laser pulses (laser fluences of 2.5 and 3.7 J/cm^2, respectively). With longer laser pulses and large fluence (8.6 J/cm^2), the prevalent crystalline phase changed from cubic to hexagonal. For intermediate deposition conditions (long pulses and lower fluences), the co-existence of the two crystalline phases was recorded. In addition, the admittance measurements in the frequency range of 1 kHz-20 MHz evidenced the contribution of deep levels to the frequency dispersion of the capacitance and current conductance of AlN MIS structures.

1. Introduction

Aluminium nitride (AlN), a wide-bandgap semiconductor material, possesses great potential for versatile applications ranging from electronics, acoustic wave and photonic devices to antiwear coatings. Obtaining AlN films with definite structure and crystalline quality is still a challenge for most deposition techniques. Thus, extensive research is still necessary to find out how exactly the crystallographic structure and degree of crystallinity of AlN films depend on the film preparation method and conditions. AlN generally crystallizes in either the hexagonal wurtzite (h-AlN) structure or cubic zinc-blende (c-AlN) polytypes; the latter has been considered as a metastable phase based upon local density approximation calculation [1]. Theoretical investigations of the thermal conductivity of AlN have shown that the energy difference between the two kinds of phase structure of AlN is so small that both hexagonal and cubic phases are able to coexist in a realistic material [2]. Still, relevant data on the formation of each of the crystalline phases of AlN have been scant so far.

AlN films deposited by reactive radio frequency and coherent magnetron sputtering have been reported to exhibit *c*-axis oriented hexagonal structure [3,4]. A highly oriented (0001) polycrystalline h-AlN structure has been obtained by metal organic chemical vapour deposition [5]. Pulsed laser deposition (PLD) method has resulted in AlN thin films in either cubic or hexagonal phase, depending on the preparation conditions. By varying the deposition temperature and ambient pressure, different crystalline structures have been obtained. Vispute *et al.* reported the synthesis of h-AlN with (0001) orientation [6], while Wen-Tai Lin *et al.* obtained cubic AlN films [7]. The metastable c-AlN was found in films synthesized by nitrogen-ion-assisted pulsed laser deposition [8]. Our recent investigations of AlN films prepared by PLD revealed that films deposited at low laser fluence incident on target surface possess cubic polytype structure [9,10]. It has also been shown that the value of the laser fluence incident on target surface is a key parameter determining the growing film characteristics, such as the crystalline quality, optical and electrical properties. We focus with this study on the effect of incident laser fluence generated by two laser sources having different pulse durations. We tried this way to get a better insight in the actual correlation between the structure and electrical properties of AlN films and the incident laser pulse energy, duration and fluence.

Extending the findings of our previous investigations, PLD AlN thin films were analyzed by X-ray diffractometry (XRD), and the effect of the incident laser fluence on the crystallographic structure and crystallite size was discussed. Additional information was obtained from the admittance measurements performed at zero DC voltage bias and an AC test voltage at different frequencies. The frequency dispersion of the capacitance and conductance of metal-AlN-silicon capacitors was considered in relation to the deposition conditions.

2. Experimental details

2.1 Film preparation

AlN films were synthesized by PLD on p-type (100)Si wafers, cleaned by standard IC technology. Prior to deposition, the chamber was evacuated to 10^{-4} Pa and the substrates were heated up to 800°C, a temperature at which the native SiO_2 covering the wafers is known to decompose. This temperature also proved to be high enough to promote the crystalline growth of AlN films [11]. The target consisting of polycrystalline AlN with 99% purity was rotated with 0.3 Hz to avoid piercing and to ensure a clean surface during multi-pulse laser irradiation. Two pulsed KrF* excimer laser sources (λ = 248 nm) were used for the ablation of the targets. The first one, model M-1701, generated pulses of 7.4 ns, while the second, a COMPEXPro 205, delivered pulses of 25 ns duration. 20,000 subsequent pulses were applied for the synthesis of each structure. A shutter was introduced between target and substrate during the first 1000 laser pulses. In this way the impurities and defects still present on the target surface after cleaning could be collected and removed before reaching the deposition area. The films were synthesized on substrates kept during deposition at a temperature of 800°C. Two different deposition regimes have been applied: (i) laser pulse duration of 7.4 ns, repetition rate of 2 Hz, target-substrate distance of 4 cm, incident laser fluence of 2.5 and 3.7 J/cm^2, and (ii) laser pulse duration of 25 ns, repetition rate of 3 Hz, target-substrate distance of 5 cm, incident laser fluence of 8.6 J/cm^2. Accordingly, the laser intensity was in all cases similar, within the narrow range of $(3 - 4) \times 10^8$ W/cm^2. We could this way independently search on the effects of laser pulse duration and incident laser fluence. Depending on deposition conditions, the film thickness in the first case was in the range of 700-800 nm, while for the second set of experimental conditions the film thickness varied around 400 nm. This can be accounted for by the difference in the target-substrate distance in the two cases.

The AlN films synthesis was carried out in vacuum (5×10^{-4} or 10^{-3} Pa) or in nitrogen at dynamic pressures of 0.1 or 10 Pa.

For the electrical measurements, metal-insulator-silicon (MIS) capacitors with the PLD AlN films were formed by vacuum evaporation through a metal mask of Al dots on the AlN surface and a continuous Al film on the Si wafer backside.

2.2 Measurement methods

The structure and composition of the AlN films were studied by X-ray diffraction (XRD) measured with a large-angle ($2\Theta = 0 - 90°$) X-ray Philips X'Pert diffractometer working with Cu Kα radiation (λ =0.154056 nm). The XRD peaks were fitted and deconvoluted by Philips Pro'Fit commercial program. The crystalline phases were identified using the ASTM database [12]. A rough estimate of the crystallites size was made from the main

peaks broadening assuming a spherical shape and using the Sherrer's formula [13].

Admittance measurements in a wide frequency range are a powerful method for studying the electrophysical properties of investigated semiconductor structures and materials, revealing in particular the role of deep levels in charge transport through an insulator film. For this reason, the admittance measurements of MIS structures with PLD AlN films were carried out at room temperature in two frequency ranges, namely (1- 500) kHz and 500 kHz - 20 MHz, on Tesla impedance meters type BM 507 and BM 508, respectively. The impedance amplitude, $|Z_m|$, and phase angle, φ_m, were simultaneously measured. The impedance value at a given frequency was transformed to the corresponding capacitance and conductance values. Accordingly, the conductance, G_f, and capacitance, C_f, of the MIS structure were calculated from the equations:

$$G_f = \cos\varphi_m/|Z_m| - \cos\varphi_{in}/|Z_{in}|$$

and   (1)

$$C_f = (1/\omega)(\sin\varphi_m/|Z_m| - \sin\varphi_{in}/|Z_{in}|).$$

During measurements no DC voltage was applied to the MIS structures, while the AC test voltage signal frequency was varied in the above mentioned ranges. In order to obtain the accurate values for a given AlN MIS structure, the residual parallel impedance amplitude, Z_{in}, and phase angle, φ_{in}, of the sample holder were taken into account as $1/|Z_{MIS}| = 1/Z_m -1/Z_{in}$. These quantities were measured before each frequency step.

It should be noted that the value of a reference capacitance, measured at 1.59 kHz with the BM 507 apparatus differed with 0.21 % only from that measured at 1.59 MHz with the BM 508 instrument. Based upon this result, one may estimate the errors in the measured capacitance values from the quality factor $Q = \omega C_f/G_f$ of the investigated AlN-Si MIS structures. For the frequency range of (1- 500) kHz this error was 6 % and it decreased to 0.8 % for the frequency range of 500 kHz - 20 MHz.

3. Results and discussion

3.1 X-ray diffraction analysis

The analysis of the recorded XRD spectra showed that the two AlN phases, i.e. hexagonal and cubic, co-existed in the deposited films, and their volume/ratio was strongly dependent on the incident laser fluence applied on the target for the ablation process. The amount of nitrogen inside the deposition chamber had also considerable influence on the crystallinity and texture of the films. According to our previous observations [9,10], the films deposited at low laser fluences (2.5 and 3.7 J/cm^2) possess a polycrystalline structure with predominant cubic phase of AlN crystallites. The XRD patterns recorded for the AlN films deposited in vacuum revealed the presence of both crystalline phases, with a prevalence of cubic one and a strong (111) texture (Fig. 1a). The corresponding lattice parameter was a=0.4045 nm (ASTM 46-1200 [12]). The

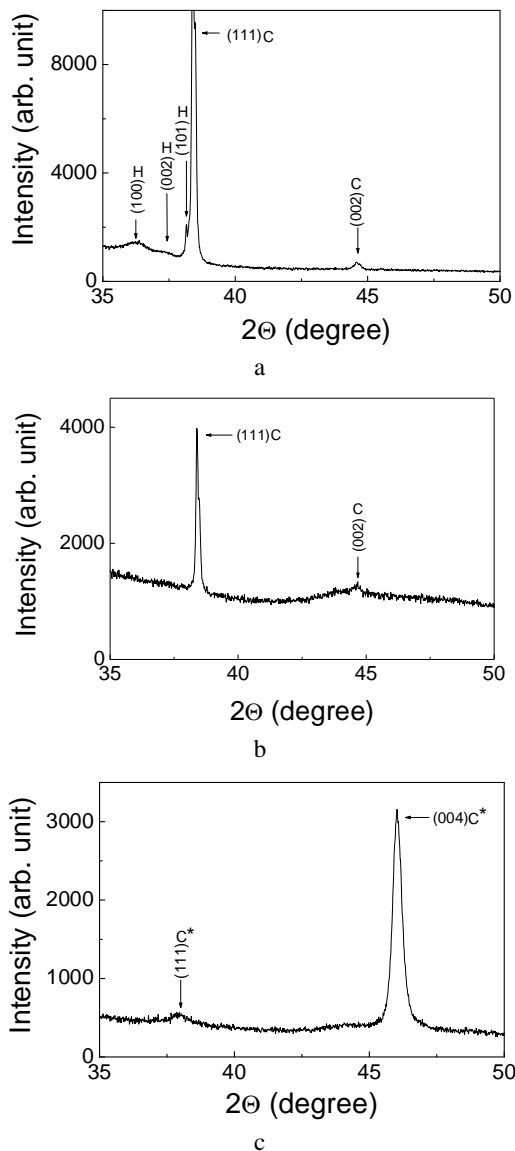hexagonal phase in these films occupied only a small volume fraction of about 2%.

Fig. 1 XRD spectra of AlN films deposited at a laser fluence of 3.7 J/cm^2 in vacuum at 5 x 10^{-4} Pa (a) and in nitrogen at a pressure of 0.1 Pa (b) and 10 Pa (c).

The deposition in nitrogen ambient resulted in formation of cubic crystallites only, the orientation and lattice parameter of which are dependent on the ambient nitrogen gas pressure. By increasing the nitrogen pressure from 0.1 (Fig. 1b) to 10 Pa (Fig. 1c), the strong cubic (111) texture changed to strong (100) texture of the cubic phase with an almost twice larger lattice parameter, a=0.7913 nm (ASTM 34-0679 [12]). A similar structure was detected in PLD AlN films obtained at a substrate temperature of 630°C and nitrogen gas pressure of 20 Pa [14].

For our AlN films, the full width at half maximum (FWHM) of the diffraction peaks varied from 0.15° to 0.2° and the corresponding mean crystallite size, estimated by Sherrer formula [13] assuming a spherical shape, was in the range of (35-50) nm.
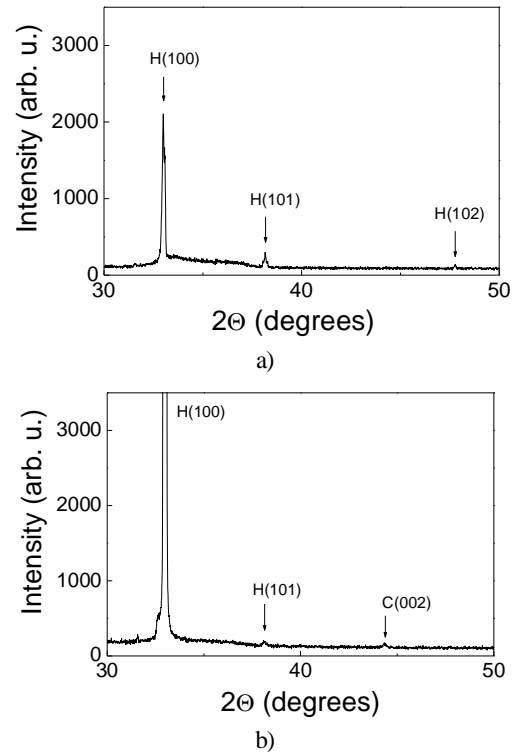

Fig. 2 XRD spectra of AlN films deposited at a laser fluence of 8.6 J/cm^2 in vacuum at 10^{-3} Pa (a) and in nitrogen at a pressure of 10 Pa (b).

By contrast, in the AlN films deposited at the highest incident laser fluence of 8.6 J/cm^2, the hexagonal structure was dominant with a strong (100) texture and lattice parameters having the values a=0.31114 nm and c=0.49792 nm (ASTM 25-1133 [12]). For illustration, Fig. 2 represents the XRD spectra of films deposited at 10^{-3} Pa and 10 Pa. In the case when the film was deposited in vacuum (10^{-3} Pa), the profile fitting and decomposition of the XRD patterns (Fig. 2a) revealed a broad peak related to the presence of amorphous phase. The volume fraction of the amorphous phase in the hexagonal AlN crystalline matrix was determined from the integrated intensities ratio of the amorphous and crystalline phases and it was ~11%. Although the XRD patterns of AlN films deposited at a dynamic nitrogen pressure of 10 Pa indicated a small amount of cubic phase (Fig. 2b), at lower pressures the hexagonal crystalline phase only could be detected.

For the films deposited at low ambient pressure (10^{-3} Pa), the FWHM of the diffraction peaks was of 0.16° which corresponds to a mean crystallite size of 50 nm. The deposition at 10 Pa nitrogen gas pressure resulted in a drastic improvement of the crystalline quality, as the FWHM decreased significantly to 0.054°. The crystallites

grew up to a much bigger size of ~100 nm, as estimated from the corresponding peak broadening. Apparently, at these definite deposition conditions a high-quality hexagonal AlN structure with prevalent (100) oriented crystallites, matching well to the underlying (100)Si substrate, could be produced. These results are consistent with other studies on PLD growth of AlN films in conditions close to ours, resulting in epitaxial AlN material with hexagonal structure [6].

The analysis of these XRD spectra experimentally proved the theoretically predicted [2] co-existence of hexagonal and cubic phases in the AlN films, and demonstrated the strong dependence of the crystalline phase and texture of polycrystalline films on the incident laser fluence on the target surface and amount of nitrogen in the ambient gas during deposition of the AlN films. By varying the incident laser fluence, either entirely cubic or hexagonal polycrystalline AlN films could be produced.

3.2 Admittance measurements of AlN MIS structures

In the previous section it was shown that depending on deposition conditions AlN films with different structures were produced. Such a structural difference could lead to various kinds of defects in the films, generating deep levels in the forbidden gap and thus making the capacitance of AlN MIS capacitors sensitive to the test signal frequency. In order to ascertain the influence of deep levels, the frequency-dependent admittance measurements at zero DC bias voltage were performed in a wide frequency range of 1 kHz- 20 MHz. The results are summarized in Figs. 3 and 4.

In Fig. 3, typical AC capacitance, $C_f(\omega)$, dispersion curves are presented as a function of angular frequency, $\omega=2\pi f$, where f is the test voltage frequency in hertz. The general trend of the dispersion curves is that three particular frequency regions could be distinguished when increasing the test frequency: a first region with decreasing C_f values, followed by a region with approximately constant C_f values and a region with further decreasing C_f values. The exception is for AlN films deposited at 0.1 Pa nitrogen pressure, for which in the first low-frequency region the capacitance C_f gradually increases with the frequency from 1.6 to 470 kHz, while keeping constant above 470 kHz (Fig. 3b). The largest C_f values were measured in MIS structures with AlN films deposited in vacuum. It has been established that nitrogen vacancies produced deep donor levels responsible for electron conduction in AlN films [15]. It can be expected that by increasing the nitrogen pressure during deposition, the concentration of nitrogen vacancies in the films and, consequently, the contribution of deep levels to the capacitance of the investigated AlN MIS structures decreases.

For the studied AlN MIS structures, the dependence of AC conductance, $G_f(\omega)$, on the test signal frequency could be characterized by two distinct frequency ranges. A wide frequency region up to ~10 MHz is characterized by a slow increase of the G_f value, followed by a region with a sharp increase of the G_f value. Such a frequency-dependent conductivity is a distinctiveness of the so-called universal AC conductivity caused by trap-to-trap hopping of charge carriers [16].
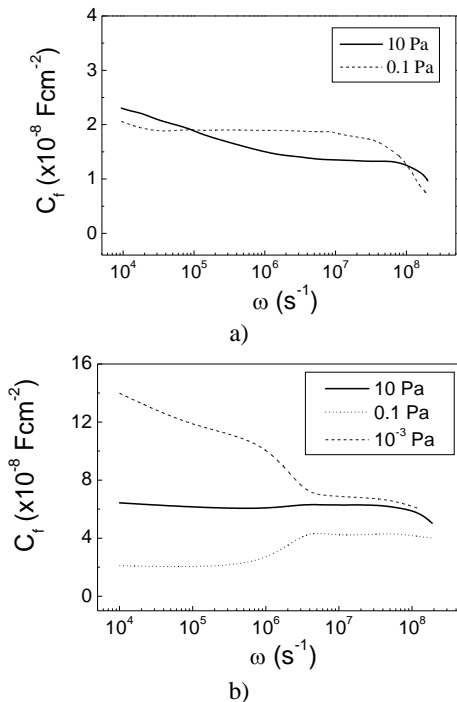

Fig. 3 Capacitance dependence as a function of test frequency measured under AC test voltage and zero applied DC bias on MIS structures with PLD AlN films deposited at laser fluences of 2.5 J/cm² (a) and 8.6 J/cm² (b) and at different ambient gas pressures.
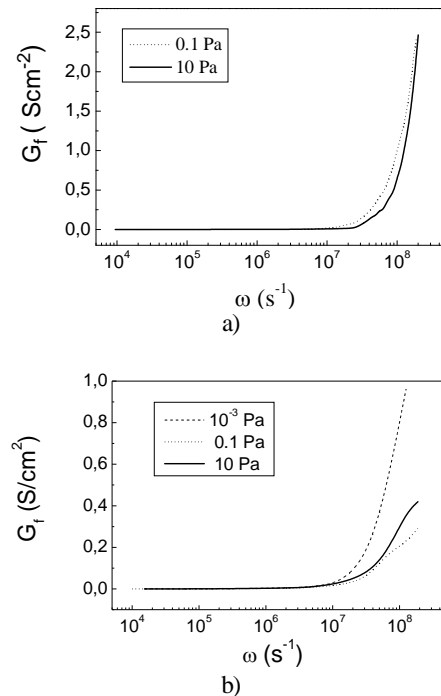

Fig. 4 Conductance dependence as a function of test frequency measured under AC test voltage and zero applied DC bias on MIS structures with PLD AlN films deposited at laser fluences of 2.5 J/cm² (a) and 8.6 J/cm² (b) and at different ambient gas pressures.

In Fig. 4, typical dispersion curves of $G_f(\omega)$ versus angular frequency ω are presented. As can be seen, considerably higher current through the MIS structures was registered in the cases when the films were deposited at low incident laser fluence (Fig. 4a). According to the XRD results, these AlN films possess cubic crystalline structure, which maybe is more defective and, hence, the contribution of defects related to deep levels to conductance current is larger. When using a fluence of 8.6 J/cm^2, the conductance current through the AlN films synthesized in vacuum was higher in comparison to films deposited in nitrogen gas ambient. This is in good correlation with the observed highest capacitance values (Fig. 4b) of this AlN MIS structure. These results are an evidence for the highest density of deep levels in MIS structure with AlN films deposited in vacuum.

The results of the frequency-dependent admittance measurements at zero DC bias voltage clearly indicated how deep levels contribute to the films capacitance and conductance values in the PLD AlN films. These states are related to defects of nitrogen vacancies responsible for electron conduction in the AlN films.

4. Conclusions

We studied the structure and electrical properties of AlN thin films synthesized by PLD in vacuum and low-pressure nitrogen under the action of two pulsed KrF* excimer laser sources generating pulses of 7.4 and 25 ns, respectively. The incident laser intensity was set in all cases at $(3-4) \times 10^8$ W/cm^2, which allowed us to discriminate the effect of incident laser fluence, varying from 2.5 to 8.6 J/cm^2, upon the properties of obtained films. A strong influence of the incident laser fluence on the structure of AlN films was established and the co-existence of the cubic and hexagonal phases was experimentally confirmed by XRD measurements. At low laser fluences (2.5 and 3.7 J/cm^2) the films had a prevalent cubic polycrystalline structure, which changed to the prevalent hexagonal one at high laser fluence (8.6 J/cm^2). We could thus evidenced that the increase of energy/fluence at a given incident laser intensity is able to gently promote the phase change (from cubic to hexagonal) of the deposited AlN films. The pressure of nitrogen in the deposition chamber had also considerable influence on the crystallinity and texture of the film structure. These results confirmed the possibility of controlled synthesis of either cubic or hexagonal crystalline AlN films by pulsed laser deposition for various applications.

By applying frequency-dependent admittance measurements of AlN MIS structures at zero DC bias voltage, the existence of frequency regions of constant capacitance was established, where deep levels did not influence the capacitance measurements. It has been suggested that deep levels of nitrogen vacancies are responsible for electron conduction in these PLD AlN films.

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