High-rate etching of single oriented AlN films by chlorine-based inductive coupled plasma for vibrational energy harvesters

H. H. Nguyen, L. Van Minh and H. Kuwano
New Industry Creation Hatchery Center, Tohoku University, Japan
hung@nanosys.mech.tohoku.ac.jp

Abstract. This paper presents our development of a high-rate etching process for fully (0002)-oriented AlN films by using a chlorine-based inductively coupled plasma (ICP) and Ni thin films as hard masks. The influences of etching characteristics (etching rate, selectivity) on various parameters (etching power, pressure and gases mixture) were systematically investigated. We achieved etching rate of 723 nm/min, the highest value that has been developed for single-oriented AlN. Etching selectivity was optimized and reached ~ 11, in this report. X-ray photoelectron spectroscopy measurements (XPS) offered a deep understanding of the etching processes and revealed the etching mechanism of AlN by chlorine for the first time.

1. Introduction

Lead-free piezoelectric materials based vibrational energy harvesters (VEHs) have become one of the novel approaches to self-sustainable power sources for the Internet of Things (IoT) [1–3]. Among the structures have been developed, aluminum nitride (AlN) thin film sandwiched between metal electrodes is the most preferable architecture for VEHs [4]. One of the key requirements for the fabrication of VEHs is the development of a well-controlled dry etching technique for patterning of the device structures. High performance and miniaturization of VEHs continued the quest for a better etching process of AlN. However, it is critical to etch AlN by using the conventional dry etching methods due to the strong ionic bonding of aluminium and nitrogen ions (~ 11.52 eV per atom) [5–7].

On the other hand, etching single oriented AlN is more challenging compared to that of polycrystal/bulk AlN [8] since the AlN films with poorer crystallinity will have a greater number of weakened or defective bonds which are more susceptible to be attacked by the etching species. Khan et al. reported that polycrystal AlN film can be etched by using BCl3/Cl2/Ar plasma at high rate of ~ 450 nm/min [5]. However, getting such high etching rate for single crystal AlN is still problematic. By using Cl2 plasma, Engelmark and Bliznetsov et. al can get the highest etching rate for highly crystalline AlN thin films of ~ 200 nm/min [7,9]. Fluorine-based etching processes have been also studied for AlN thin films. The biproduct, however, of etching processes that contains Al and F, is hard to be volatilized [7,10].

In this study, to achieve high etching rate of fully (0002)-oriented AlN thick films (~ 5 µm), we employed chlorine/argon-based reactive ion etching (RIE), and to increase etching efficiency, an ICP chamber was utilized. By tailoring the ICP, a horizontal electrical field was created by RF coils, inducing an intensive magnetic field in the vertical plan which converges etching radical to the center of the chamber and generates a high-density plasma. To understand etching mechanisms behind these processes, high resolution XPS measurements on a film under etching will be studied.
2. Experimental

The (0002)-oriented AlN film (~ 5.1 µm) was developed on a (100) silicon substrate by using an alternative current (AC) magnetron reactive sputtering (AMS212-1-S) [11]. To obtain highly crystalline AlN film, the Si substrate was cleaned by sulphuric acid/hydrogen peroxide/DI water mixture (SPM) prior the deposition. Base pressure of the sputtering chamber was maintained at less than $3 \times 10^{-7}$ Torr [11,12]. A 500-nm Ni thin film was deposited on top of AlN by a radio frequency (RF) magnetron sputtering (Shibaura CFS-4ES-II) to be served as a hard mask. The crystallinity of the as-deposited Ni/AlN film was investigated by X-ray diffractometer equipped with a two-dimensional detector (2D-XRD, Bruker D8 Advanced) [13]. Thin film thickness and etching depths were controlled by a nanometric (NanoSpec 3000) and a surface profiler (Tencor P-10), respectively.

In this study, the Ni thin film was patterned to form etching mask by an electrochemical setup using a DC power supply (KEITHLEY 2401) and a pure Ni plate (99.99%, Nilaco Co., Ltd.) as the cathode. A mixture of H$_2$SO$_4$ : H$_2$O = 4 : 3 was used as the electrolyte for Ni patterning [14]. AlN etching processes were conducted by using an ICP chamber (Samco, RIE-101iPY) in Cl$_2$/SiCl$_4$/Ar environment. The Ar gas was added to stabilize the plasma environment and partially to enhance the physical etching. The SiCl$_4$ is beneficial to protect the etching sidewall [15,16]. The etching parameters namely etching pressure, etching power, and gases flowrate can be individually monitored to optimize the process.

3. Results and discussions

XRD measurements verified the crystallinity of the deposited Ni/AlN film. Figure 1a shows a 2D-XRD pattern of the as-deposited Ni/AlN films on Si substrate. Except the diffraction peaks of Si (400) from substrate and Ni (111) from mask, only peaks from (0002) and (0004) planes of AlN were observed on the pattern, indicating the AlN film has c-axis orientation. Full width at half maximum (FWHM) of (0002) AlN rocking curve was measured of 1.48° (Figure 1b), that confirmed the highly crystalline AlN film was successfully deposited.

![Figure 1. 2D-XRD pattern of the as-deposited Ni/AlN film (a) and the rocking curve of the (0002) AlN peak at diffraction angle $\theta = 18.02^\circ$ (b).](image)

Figure 2 reveals the influences of etching rate and selectivity of AlN to Ni mask on gas flowrates, ICP power and etching pressure. The Ar and SiCl$_4$ gas flowrates were firstly investigated while the Cl$_2$ flowrate, ICP/Bias power and etching pressure were kept constant at 20 sccm, 500W/200W and 3 Pa, respectively (figure 2a, b). As can be seen from figure 2a, increasing the Ar flowrate larger than 3 sccm will significantly decrease the etching rate and selectivity since the etching rate of the Ni mask is strongly depended on the Ar bombardment of the thin film surface. Similarly, the etching rate and selectivity raised with SiCl$_4$ concentration and reached the highest value at ~ 13% of SiCl$_4$ in Cl$_2$/Ar mixture. If
SiCl₄ flowrate exceeds the aforementioned value, a slower etching rate is observed (Figure 2b) due to the reduction of reactive species (Cl⁻) in the chamber [17].

The dependences of etching rate and the selectivity on ICP power and etching pressure were shown in Figure 2c and 2d. The etching rate increased linearly with etching power and achieved the highest value for single oriented AlN of 723 nm/min at power of 800 W (Figure 2c). Highly selective etching can be obtained with ICP power of 600 W and chamber pressure of 3 Pa, corresponding etching rate and selectivity were ~ 475 nm/min and 11, respectively (Figure 2d).

Figure 3 presents an etching profile of the 5.1-µm AlN film. The film thickness, side wall angle and the value of side etching can be confirmed by the FE-SEM image. Sidewall angle and side etching were 71° and 1.8 µm, respectively, at the etching pressure of 3 Pa and ICP power of 600 W. The surface of AlN film has been bombarded by etching species since the 500-nm Ni mask was just enough for etching of 5.1 µm AlN. To protect the surface of AlN film, a thicker than 500-nm thickness mask is needed. Furthermore, at the toe of the etching wall, an over-etched region on silicon substrate was observed. The region can be ascribed to the high bias power (200 W) that made etching species reflected to the substrate when they reached to the film surface. The similar as-symmetry etching profiles were also observed by Schaepkens et al. who performed SiO₂ etching by fluorocarbon plasma [18,19].

Figure 4 shows an XPS survey scan on a half-thickness-etched AlN surface. A considerable amount of residue silicon and chlorine were observed on surface of etched film. Absorbed oxygen and nitrogen atoms were also found on the surface however those atoms can be easily removed by Ar sputter.
Figure 3. Cross-sectional view FE-SEM image of 5.1-μm etched AlN film on Silicon substrate at ICP power of 600 W, etching pressure of 3 Pa.

Figure 4. XPS survey scan of half-thickness-etched AlN surface. Oxygen and Nitrogen were mainly absorbed from outside environment.

High resolution XPS scans of the Al2p and N1s peaks revealed the AlN etching mechanism (Figure 5). These XPS analyses were performed on the surface of a half-thickness-etched film and gradually down to the depth of 25 nm by using an integrated ion gun (Ar) that bombards the sample during the measurements. As can be seen on figure 5a–f, Al2p peak gradually shifted from 76.2 eV to the Al-N bonding at binding energy of 74.7 eV [3,20]. These spectrums can be deconvolved into three Gaussian-Lorentzian subpeaks namely Al-N, Al-O and Al-Cl. The intensities of Al-O and Al-Cl subpeaks gradually decreased when the measurement depth increased. These XPS measurement results supported the formation of the etching by-product of AlClₓ which can be volatile by Ar ions under high bias power. On the other hand, these by-products were remained on the sidewall of etching thin film that prevent further horizontal etching. Ideally, the sidewall of the etching film will not be bombarded by the Ar ions.

Figure 5. High resolution XPS spectra of Al2p (a – f) and N1s (g – l) spectra at different measurement depths (0 nm – 25 nm). Dotted lines denote for the deconvolution peaks, number in the box represents for the XPS measurement depth.
Similarly, N1s peak can be deconvoluted into 3 subpeaks corresponding to N-Al, N-O and N-C bonding (figure 5g – l). The peaks which were assigned to the N-O and N-C bonds, gradually be neglected when we increased the measurement depth, leaving only N-Al bonding at binding energy of 397.3 eV [3,20] on the film surface.

4. Conclusion
In summary, a high-rate etching process for single-oriented AlN film was successfully developed in this paper. The highest etching rate of 723 nm/min thus far introduced for highly crystalline AlN was achieved at ICP power, pressure and gases flowrate of 800 W, 3 Pa and Cl2:SiCl4:Ar = 20:3:3 (sccm), respectively. We, for the first time, demonstrated the dry etching process for a thick, single-oriented AlN film (5.1 µm) by chlorine-based ICP-RIE. The etching angle and side etching were 71° and 1.8 µm, respectively. By the investigations on the etching surface using high resolution XPS measurements, etching mechanism was proposed and discussed through the paper. These results will contribute to the understanding of etching AlN and to construct basis for high output power VEHs fabrication process.

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