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Surface acoustic wave properties of natural smooth ultra-nanocrystalline diamond characterized by laser-induced SAW pulse technique

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Abstract

Diamond is one of the best SAW substrate candidates due to its highest sound velocity and thermal conductivity. But conventional diamond films usually express facet structure with large roughness. Ultra-nanocrystallined diamond (UNCD) films grown in a 2.45 GHz IPLAS microwave plasma enhanced chemical vapor deposition (MPECVD) system on Si (100) substrates in CH_4-Ar plasma possess naturally smooth surface and are advantageous for device applications. Moreover, highly C-axis textured aluminum nitride (AlN) films can be grown by DC-sputtering directly on UNCD coated Si substrate. However, properties of UNCD films are much complex than microcrystalline diamond films, that is because this is a very complex material system with large but not fixed portion of grain boundaries and sp^2/sp^3 bonding. Properties of UNCD films could change dramatically with similar deposition condition and with similar morphologies. A simple and quick method to characterize the properties of these UNCD films is important and valuable. Laser-induced SAW pulse method, which is a fast and accurate SAW properties measuring system, for the investigation of mechanical and structure properties of thin films without any patterning or piezoelectric layer.

Keywords: UNCD; Nano-diamond; SAW; Laser-induced SAW pulse technique

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1. Introduction

Surface acoustic wave (SAW) devices, offering a high degree of frequency selectivity with low insertion loss in compact size [1], are important in tele-communication applications. However, the operation frequency of a SAW device is closed related to the spacing of interdigital transducer (IDT), which is significantly limited by the photolithograph capability [2]. A possible route to increase the operating frequency of such devices is to use a substrate material, which supports a faster SAW propagation, such as diamond [3,4], sapphire [5] or SiC [6]. While possessing the highest sound velocity as well as the highest thermal conductivity, diamond is nearly an ideal substrate material for high frequency & high power SAW applications. But the diamond films synthesized by conventional chemical vapor deposition (CVD) technique contain a faceted granular structure with large roughness [7]. Post-polish, which is required to render the surface of the diamond films smooth enough for fabricating the devices, is time consuming, complex and costly [8]. Another possible solution for developing high frequency SAW applications is to utilize the ultra-nanocrystalline diamond (UNCD) films, which have naturally smooth surface, while possessing high acoustic velocity [9,10]. The question remains is whether the presence of abundance of grain boundaries in UNCD films will hamper the propagation characteristics of surface acoustic waves or not. Therefore, the application of a proper technique for characterizing the acoustic wave propagation behavior is necessary. Conventional technique for evaluating the propagation behavior of the surface acoustic wave is based on the frequency response of a SAW device, which is more complicated and is usually influenced by the device structure.

The laser-induced SAW pulse method can directly investigate the SAW-related (i.e. mechanical and structural) properties of thin films [11,12] without the necessity of preparing a

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piezoelectric layer or patterning an interdigital transducer (IDT) structure. And most important, it doesn't need such thick enough diamond films to neglect Si effects. Using theoretical calculation, the effect of Si substrate could be considered and the properties of NCD or UNCD film could be restored. It is a fast and accurate SAW-based measuring technique, which is very suitable for characterization of acoustic wave propagation effects in thin film systems [13]. This technique is thus adopted in this paper for examining the propagation behavior of surface acoustic waves on UNCD films grown on (100) Si-substrates. The factor influencing these behaviors will be discussed.

2. Experimental

The UNCD films were grown on Si (100) substrates by a microwave plasma enhanced chemical vapor deposition (MPECVD) process, using a 2.45 GHz plasma source system (IPLAS, Cyrannus). The Si substrates were first pre-carburized in CH_4/Ar plasma (0.8% CH_4/Ar), and then ultrasonicated with a solution containing diamond (10 nm) & Ti (~50 nm) powder mixture, which is designated as PC–U process. The detail discussions of PC–U pre-treated method were published elsewhere [14]. The UNCD films were deposited on the pre-seeded substrates by using MPECVD process again, to a thickness of ~2.0 and ~6.2 μm. The aluminum nitride (AlN) films were then DC-sputtered on UNCD films directly with DC power 300 W, 0.4 Pa, and 50 sccm N_2 flow at 300 °C to a thickness of ~3.5 μm. The structure, morphologies, and bonding structures of these films were characterized by X-ray diffractormetry (XRD, Rigaku), scanning electron microscopy (SEM, Joel), atomic force microscopy (AFM), Raman spectroscopy (Renishaw, RA100) and NEXAFS in Synchrotrom techniques. The adhesion between UNCD and Si substrate was determined by a ramping-load-scratch-test using nanoindenter instrument equipped with a nanoscratch capability (MTS, USA). The present test employed a Berkovich diamond tip oriented in the face forward mode. During the scratch-test, the load and the penetration depth were measured and recorded by the nanoindenter.

The laser-induced SAW pulse technique was used for characterizing both, SAW propagation and mechanical properties of UNCD films. The setup of the apparatus for such a measurement is schematically illustrated in Fig. 1. A pulsed laser beam (N_2-laser @ 337.1 nm, 0.5 ns duration) is focused on the substrate surface by a cylindric lens in order to excite a line-shaped broadband SAW pulse via a thermo-elastic mechanism. A piezoelectric PVDF polymer foil, pressed onto the sample surface by a sharp steel wedge (width ~5 μm), is used as a broadband sensor for detecting the SAW pulse propagated along the surface of the thin film system. After detection the SAW pulses will be amplified, digitized by an oscilloscope and converted to complex valued spectra (i.e. amplitude and phase spectra) by a fast Fourier transform algorithm. If this is done for different well-known propagation lengths on the one hand the SAW phase velocity dispersion can be determined very accurately from the accompanying phase spectra. Knowledge of the velocity dispersion of a film system is a key feature, because it gives the possibility to recover the material parameters (e.g. elastic constants, mass density and film thickness) with an appropriate fit procedure. On the other hand the damping of the amplitude spectra with increasing propagation length can deliver an estimation of SAW propagation losses due to scattering at thin film imperfections. If the evaluation is performed without the piezoelectric foil (i.e. only with the bare steel wedge) the strength

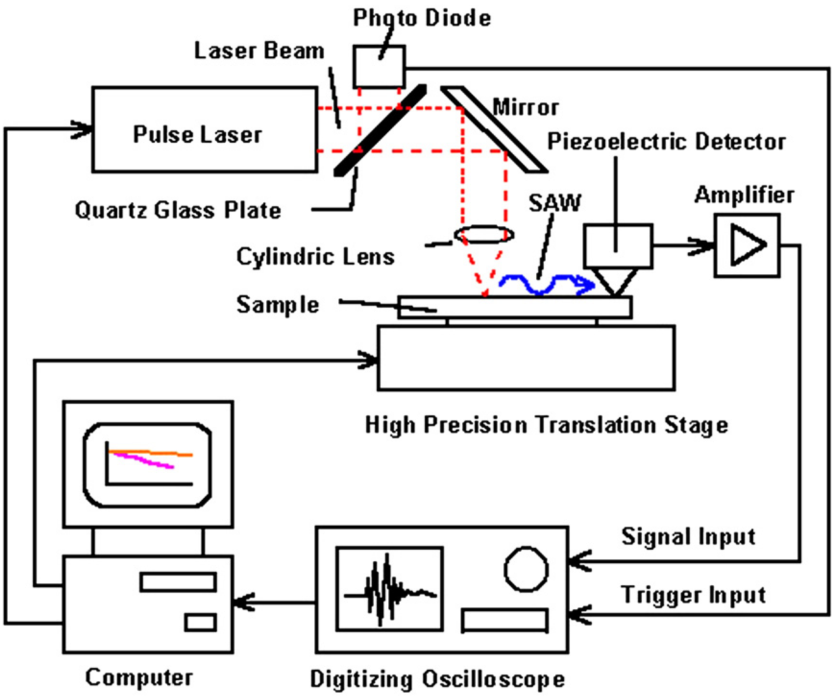

Fig. 1. Schematics showing the setup of laser-induced SAW pulse technique for characterizing SAW and mechanical properties for UNCD films.

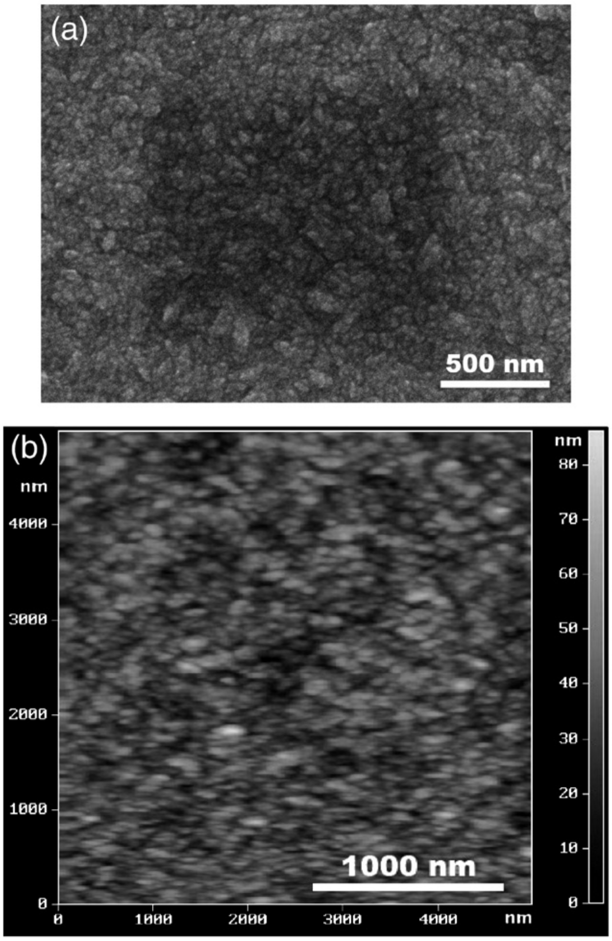

Fig. 2. (a) SEM and (b) AFM micrographs of UNCD films grown for 3 h on silicon substrates pretreated by PC–U process, which is pre-carburization and then ultrasonication with diamond/titanium powder mixture.

of the obtained electric signal gives a measure of the piezoelectric capability of the film system. Laser-induced SAW pulse measurements were performed at room temperature on two UNCD/Si samples with different film thicknesses for determination of the Young's modulus of UNCD, while a third sample additionally covered with an AlN layer was checked for their piezoelectric behavior.

3. Results and discussion

The morphologies of the UNCD films grown on Si-substrates varies pronouncedly with the nucleation technique and the chemistry in the plasma used for synthesizing the films. The diamond nuclei can hardly form on bare Si-substrates subjecting no pre-seeding treatment process. The UNCD films grown on such an untreated substrate are very rough and poorly adhered to the substrate. Only when the substrates were properly pretreated and the films were grown in H_2-deficient plasma (e.g. Ar-plasma), can a film containing nano-sized grains with very smooth surface be obtained. Fig. 2(a) and (b) are the SEM and AFM micrographs, respectively, showing the typical surface morphology of UNCD films deposited on PC–U processed substrates. Nucleation density of UNCD films deposited on the PC–U substrates reaches $\sim 1\times10^{11}$ clusters/cm^2. Thus obtained UNCD films contain diamond grains of roundish geometry and with a size less than 10 nm, possessing a smooth surface, i.e., rms ~8.8 nm.

Fig. 3(a) represents the sliding wear tracks on PC–U nucleated UNCD films resulted by nano-scratching testing procedures. It shows clear critical point, where the UNCD films started to delaminate from substrate. Fig. 3(b) shows the penetration profiles of ramping load nano-scratch surface for UNCD films grown on substrates pretreated by PC–U process, where the surface penetration is plotted as a function of the applied load. During the nano-scratching test, the Berkovich tip gradually penetrated through the UNCD films due to the linearly increasing load. The profile drops suddenly when the films delaminate from the substrate. The load at which the Berkovich tip suddenly drops is designated as critical load (L_c). The critical load is estimated as ~22 mN for the UNCD/(PC–U)Si films, illustrating that thus obtained UNCD films adhere very well to the Si- substrates.

Fig. 4(a) and (b) shows the Raman and NEXAF spectra of UNCD films, respectively. There are four major Raman resonance peaks observed at around 1150 cm^{-1} (ν_1), 1350 cm^{-1} (D), 1480 cm^{-1} (ν_3) and 1580 cm^{-1} (G) in Raman spectrum of UNCD films taken by visible laser (513.6 nm, Fig. 4(a)). The Raman peaks for UNCD films are much broadened, which is presumably

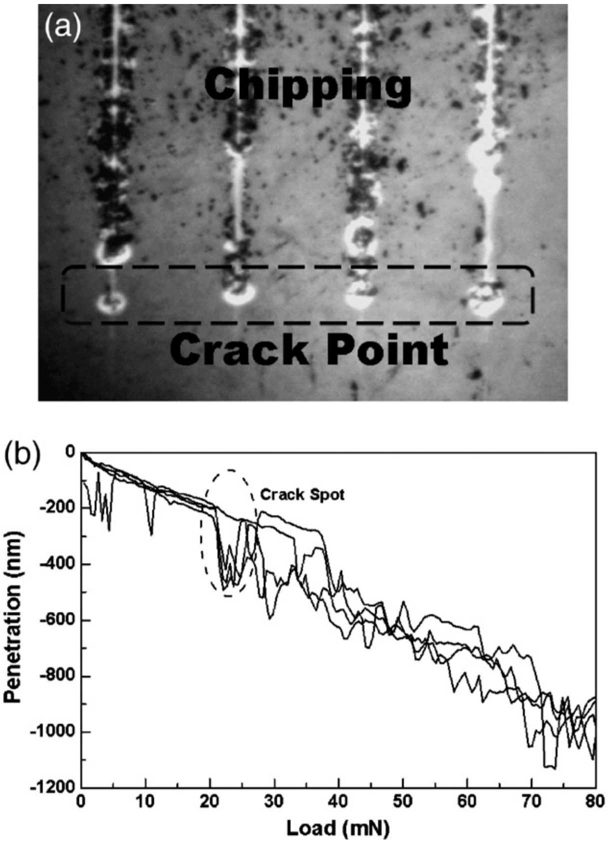

Fig. 3. (a) The micrograph showing the typical damaged image in ramping-load-scratch-test, after nano-indentor tip scratching of UNCD films grown on silicon substrate and (b) the penetration curves of the nano-indentor tip scratching along UNCD films.

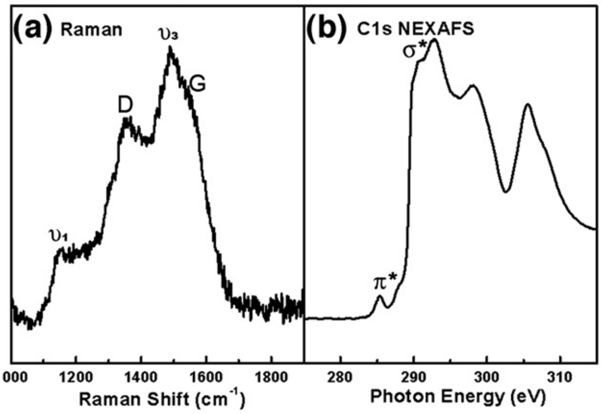

Fig. 4. (a) Raman spectra and (b) NEXAFS of UNCD films grown for 3 h on silicon substrates pretreated by PC–U process, which is pre-carburization and then ultrasonication with diamond/titanium powder mixture.

due to the smallness in diamond grains and the presence of transpolyacetelyne [15] in the grain boundaries of the UNCD films. Even though the Raman signal is much more sensitive to the sp^2-bonded carbon than to the sp^3-bonded one, such that sharp peak at 1332 cm^{-1} is usually no longer observable for UNCD films, these Raman spectroscopy is still a signature indicating that the grains in NCD and UNCD films are of sp^3-bonded nature [16]. Both NCD and UNCD films shows very similar Raman spectra even they are deposited in very different condition, in which NCD may be deposited in methane-hydrogen plasma and UNCD films are deposited in methane-argon plasma. However, another technique is required to unambiguously identify that the UNCD films do contain grains of diamond nature.

The NEXAFS using synchrotron radiation technique is thus utilized to characterize the bonding structure for diamond films with nano-sized grains, as the sensitivity of Synchrotron radiation to sp^3-bondings in NEXAFS is comparable with those to sp^2-bonding. The NEXAFS spectra shown in Fig. 4(b) reveal the typical sp^3-bonding at 289.7 eV, a characteristic of C(1s)-σ* peak and 302.5 eV dip related to second absorption band gap of sp^3 structure. A weak NEXAFS peak around 285.4 eV, which was designated as the C(1s)-π* transition, corresponds to sp^2 graphite-like carbon. It indicates low sp^2-content for these UNCD films. The graphite-like carbon is believed to distribute along the grain boundaries.

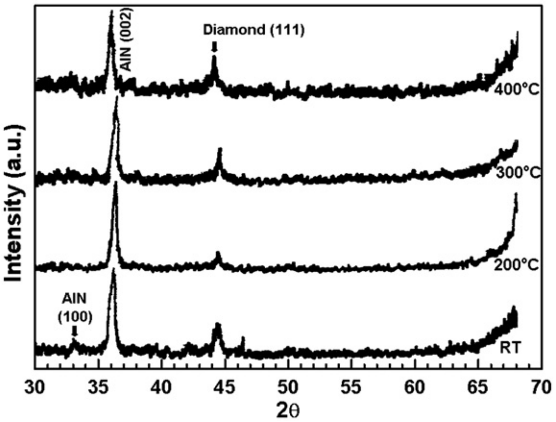

Fig. 5. XRD patterns of AlN films grown directly on UNCD films by DC sputtering process.

The surface of UNCD films is smooth and is compatible with AlN materials, such that the AlN films can be deposited directly on UNCD surface. Fig. 5 shows the XRD diffraction patterns of AlN/UNCD/Si layered films deposited at different substrate temperature. This figure indicates that the diamond films are (111) oriented. Polycrystalline AlN films were resulted when AlN films were deposited on UNCD/Si substrates at room temperature, viz. a weak AlN[100] is also present in addition to the AlN[002] peak. When the substrate temperature was higher than 200°C, only AlN [002] was observed at $2\theta = 30\sim65°$ beside the diamond [111] peak, indicating that the AlN films are highly (002) preferred oriented. It should be noted that such a highly textured AlN film can be obtained only when the diamond surface is smooth enough, i.e., rms < 20 nm. The plain view morphology of AlN films on UNCD surface is revealed by the SEM and show smooth and uniform morphologies. The cross section view of AlN films shows the column structure with closely packing for the films (not shown).

Fig. 6 shows the laser-induced pulse SAW measurement results. There are three samples which were investigated; (i) thin UNCD (∼2 μm)/Si (Curve I), (ii) thick UNCD (∼6.2 μm)/Si (Curve II), and (iii) AlN (∼3.5 μm)/UNCD (∼6.2 μm)/Si (Curve III). The thick and thin UNCD films were prepared with the same deposition condition only with different deposition time. When a surface acoustic wave propagates along the surface of a solid body its penetration depth is roughly comparable to the acoustic wavelength [17]. For this reason in a layered system the influence of the film and the substrate on the SAW propagation is strongly dependent on the SAW wavelength (or on the frequency). In other words, the effect of Si substrate on the SAW is strongly correlated with film thickness to wavelength ratio ($h_{\mathrm{film}}/\lambda_{\mathrm{SAW}}$).

Because of the fact, that a [110] propagating SAW on an uncovered (100) Si substrate is much slower in comparison with a SAW on UNCD or on AlN, respectively, the total SAW velocity of the layered structure increases with an increasing $h_{\mathrm{film}}/\lambda_{\mathrm{SAW}}$ ratio. For a given film thickness this behavior results in a faster SAW at higher frequencies. In the UNCD/Si system the film tends to

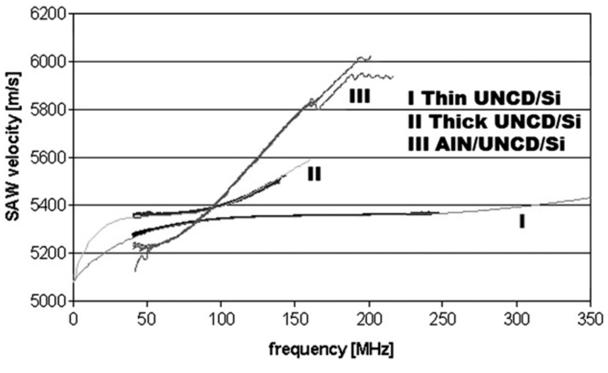

Fig. 6. The SAW propagation characteristics measured by pulsed laser technique (thick lines) with accompanying fit curves for material data extraction (thin lines).

stiffen the surface and so the SAW velocity starts to increase from the value of pure Si substrate until it reaches a plateau-like region when the relative film thickness $h_{\mathrm{film}}/\lambda_{\mathrm{SAW}}$ is between ~0.04 and 0.11 for all of the three samples. Thicker films with $h_{\mathrm{film}}/\lambda_{\mathrm{SAW}} > 0.11$ tend to dominate again and lead to a further increase of the SAW velocity. Therefore for a significant increase of SAW velocity (or frequency capability of a SAW device) the relative UNCD film thickness should be much thicker than 0.11 λ_{SAW}. From the measured SAW velocity curves depicted in Fig. 6 the acoustic film properties were determined. With properly fitting of these laser pulse data, both the thin and the thick UNCD films show very similar Young's modulus ~550 GPa, with an accompanying Poisson ratio of 0.286 and UNCD density of 3.1 g/cm^3. This result also proves that using a theoretical fitting, the effect of Si substrate could be considered and the properties of NCD or UNCD film could be restored, even the SAW energy also penetrate into the Si substrate. All three samples showed no significant SAW propagation losses. It should be mentioned, that a sufficient piezoelectric characteristics of AlN film was verified, when measured AlN/UNCD/Si layered structure without piezoelectric polymer foil.

4. Conclusion

Highly (002) oriented AlN film can be deposited directly on UNCD surface, possessing good piezoelectric properties. Laser-induced pulsed method is used for characterizing SAW and mechanical properties of UNCD films. In this article, we want to introduce this simple and quick method to characterize SAW properties of NCD or UNCD films without complex patterning or very thick diamond film. Such a simple method could use for easily finding out the relationship between deposition parameters and SAW properties of NCD or UNCD films. And combined with structure analysis from SEM or even TEM, bonding structure analysis from Raman or NEXAFS, a whole picture of NCD or UNCD material system for SAW application could be build.

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