Nanocrystalline diamond enhanced thickness shear mode resonator

4 AUTHORS, INCLUDING:

Oliver A Williams
Cardiff University
145 PUBLICATIONS **2,814** CITATIONS

SEE PROFILE

Vincent Mortet
Institute of Physics ASCR
96 PUBLICATIONS **1,049** CITATIONS

SEE PROFILE

Michael Daenen
Hasselt University
31 PUBLICATIONS **815** CITATIONS

SEE PROFILE

Nanocrystalline diamond enhanced thickness shear mode resonator

Oliver A. Williams,[a] Vincent Mortet, Michael Daenen, and Ken Haenen
Institute for Materials Research, Hasselt University, Wetenschapspark 1, B-3590 Diepenbeek, Belgium
and Division IMOMEC, IMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

A nanocrystalline diamond coated thickness shear mode resonator has been fabricated as an alternative to the quartz crystal microbalance. Due to the low temperature phase transition of quartz, the piezoelectric material was replaced with langasite, a piezoelectric with no phase transition up to its melting point. The resulting device shows clear resonant behavior and oscillates in both air and in liquid. The diamond coating shows clear faceting by scanning electron microscopy and sp^3 bonding by Raman spectroscopy. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2471649]

The quartz crystal microbalance (QCM) has evolved from simple thickness monitoring in vacuum deposition systems into sophisticated electrochemical and biological sensors in liquid and gaseous environments.[1] The development of dissipative QCM has allowed the simultaneous monitoring of the viscoelastic properties of attached layers with their mass loading,[2] and can be further expanded with electrochemical techniques such as cyclic and stripping voltammetry.[3] As these experimental techniques evolve in complexity, the standardization of the surface of the QCM element becomes increasingly important. Diamond is an ideal surface for many biological and electrochemical applications due to its wide electrochemical window,[4] tuneable wettability by simple stable surface terminations with nanoscale resolution,[5] low friction,[6] extreme chemical stability, and bioinertness.[7] Most significantly, the surface of diamond has been shown to be particularly stable when functionalized with biomolecules.[8] This fact makes diamond of particular interest for biosensing applications (such as QCM) where the detection of mass loading effects could be significantly affected adversely by biomolecules becoming spontaneously untethered from the sensor surface.

The coating of QCM elements with diamond has been problematic, principally due to the phase transition temperature of quartz being significantly below standard diamond growth temperatures.[9] Even with low temperature growth techniques,[10] the coating of QCMs with diamonds has not yielded a working device. This is most likely due to the piezoelectric properties of quartz deteriorating far below the actual phase transition. A diamond coated microbalance was fabricated by Zhang *et al.* who grew a freestanding diamond substrate and bonded it to a QCM element.[11] This process requires a relatively thick diamond substrate with obvious cost implications and crystal loading. In this work, to bypass the restrictions of the quartz phase transition, the quartz crystal is replaced with a high temperature stable piezoelectric. In this case, the piezoelectric langasite was chosen for its lack of phase transition up to its melting point.[12] However, there are several alternatives such as gallium phosphate and langatate.[13] As the piezoelectric material is no longer a quartz, the device is called by its more generic name, i.e., a thickness shear mode resonator.

Commercially sourced langasite oscillators with a resonant frequency around 5 MHz were used throughout. In order to facilitate diamond growth on these oscillators, a SiO_2 interlayer was deposited by magnetron sputtering to a thickness around 100 nm. The substrate was then immersed in a solution of detonation nanodiamond powder and ethanol, and was exposed to ultrasound via a standard bath for 30 min. After pure ethanol rinsing and nitrogen blow drying, the substrate was placed inside an Astex 6500 microwave plasma enhanced chemical vapor deposition reactor and was pumped down to a vacuum better than 1×10^{-3} mbar. Growth parameters were 4% CH_4 diluted by H_2, 2000 W, 25 torr, and $\sim$700 °C for 60 min. The temperature was monitored *in situ* by a Williamson Pro92 dual wavelength pyrometer. These conditions are similar to those known to grow nanocrystalline diamond in this reactor.[14] Micro-Raman measurements were done using a Dilor triple monochromator equipped with a liquid nitrogen-cooled charge coupled device detector. The incident laser light from an Ar-ion laser (514.5 nm, 200 mW) was focused on a spot size of about $1-5$ μm. Scanning electron microscopy images were taken with an FEI Quanta 200F. A schematic of the fabricated structure is seen in Fig. 1. It can be seen in this figure that the bulk wave oscillation is generated between the two metal electrodes, whereas the SiO_2 interlayer and the nanocrystalline diamond layer shift the resonant frequency somewhat due to mass loading. The frequency response of the nanocrystalline diamond coated langasite oscillator was characterized with a Hewlett Packard HP4194A impedance/gain-phase analyzer, operated in the gain-phase mode. The drive voltage was 0.125 V peak to peak.
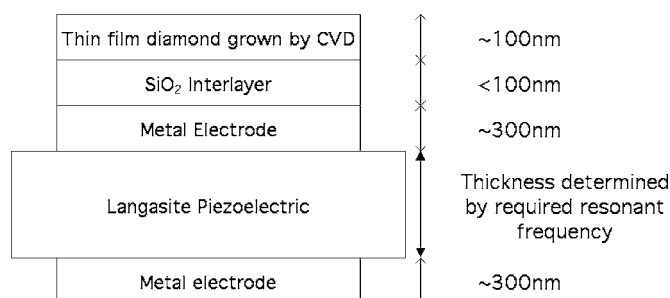

FIG. 1. Schematic of the nanocrystalline diamond coated langasite thickness shear mode resonator.

a)Electronic mail: oliverwilliams@mac.com

90, 063514-1

FIG. 3. Phase shift against frequency spectrum showing the resonance of the nanocrystalline diamond coated langasite thickness shear mode resonator.
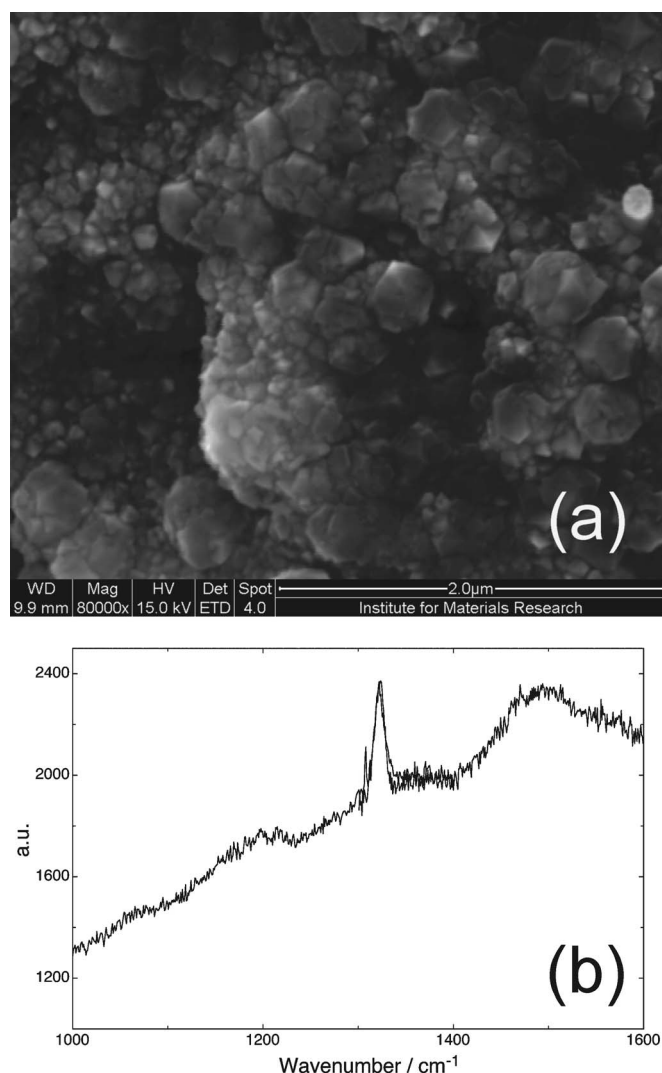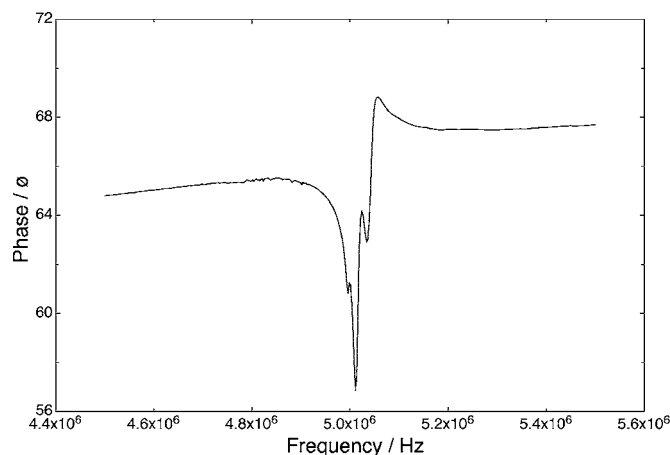

FIG. 2. (a) Scanning electron micrograph of nanocrystalline diamond coating; (b) Raman spectrum of nanocrystalline diamond coating.

The characterization of the nanocrystalline diamond film is shown in Fig. 2. Figure 2(a) is a scanning electron micrograph image showing clearly facetted nanocrystalline diamond. The grain size of the diamond film in this case is estimated at 50–200 nm, rather bigger than required with a sizeable distribution in crystallite size. The large grain size is due to the rather thick nature of the film and the high CH_4 content used during the growth of this prototype. The morphology of this film can be optimized considerably by reducing these parameters, as the film has clearly coalesced in significantly less time that the growth duration used here. The Raman spectrum of the nanocrystalline diamond coating is shown in Fig. 2(b). A pronounced peak around 1332 cm^{-1} is clearly visible, indicative of sp^3 bonding. This peak is significantly broadened due to the small crystallite size of the diamond grown here. Accompanying this peak is a small shoulder starting around 1100–1200 cm^{-1} and a band at around 1450 cm^{-1}. Both of these features are attributable to nondiamond carbon and are usually observed together. The 1150 and 1450 cm^{-1} peaks in diamond are attributed to small amounts of transpolyacetylene at the grain boundaries of nanocrystalline diamond.[15] In addition, features at 1560 cm^{-1} are attributable to disordered[16] carbon presumably also at the grain boundaries. Hence, there is evidence of

nondiamond carbon as well as diamond, as is expected for nanocrystalline diamond, due to the high volume fraction of grain boundaries.

Figure 3 shows the phase response versus frequency for the oscillator. Clear resonance behavior is observed in the phase response. However, two spurious an-harmonic resonances are observed near the resonant frequency. These are thought to be due to the high piezoelectric coupling coefficient of langasite and are not generally observed on quartz oscillators. These are also present in uncoated langasite resonators. These anharmonic resonances do not affect the operation of the resonator with a standard phase lock amplifier, as often commercially used to track the resonant frequency of QCM crystals. The resonant frequency of this oscillator is around 5.01 MHz, very near that of the virgin oscillator of 4.95 MHz, and the impedance increased from 60 to 1000 Ω. This impedance is still within the range of commercial microbalance electronics. Hence, the deposition of diamond at high temperature has not destroyed the piezoelectric effect of this material, although it has somewhat damped the oscillation and reduced the Q factor. In fact, the resonant frequency has increased very slightly from the virgin resonator, which is counterintuitive as the mass loading effect of the SiO_2 and diamond layer depositions should decrease the resonant frequency. This could possibly be due to the diffusion of the electrodes and carbon into the langasite at high temperatures. This would have the effect of effectively reducing the distance between the two electrodes, and hence increasing the resonant frequency. More experiments are required to confirm this phenomenon, but, if true, it could be rectified by using a buffer layer known to reduce diffusion, such as platinum, between the electrodes and the langasite. The broadening of the resonant peak is also, in part, due to the roughness of the surface, a factor easily improved in future structures with thinner diamond layers and better nucleation. This broadening effect could also account for the apparent upshift in resonant frequency.

The frequency response of this device can be further improved by the optimization of the device structure. Reducing the size of the electrodes will reduce the anharmonic resonances. The Q factor can also be improved by replacing the top metal electrode with a refractory metal upon which diamond can readily be synthesized, hence reducing the overall crystal load. The diffusion of electrode metal and

carbon into the langasite at high temperatures can be reduced with the choice of a suitable refractory electrode. Preliminary work has shown success with a tungsten electrode, also allowing a much thinner diamond layer due to enhanced nucleation density. This layer was boron doped for a simultaneous electrochemical access to the surface. This device resonates at 2.7 MHz, roughly half that of the device in Fig. 3. This is expected as the langasite is about twice as thick.

In summary, a nanocrystalline diamond coated langasite thickness shear mode resonator has been demonstrated. By replacing the quartz piezoelectric with a high temperature stable piezoelectric, it is possible to grow diamond at conventional growth temperatures without the loss of the piezoelectric properties of the substrate, and hence the utility of the device. This diamond coated resonator has a number of applications in bio sensing, if functionalized,[17] electrochemical microgravity,[18] and viscoelastic monitoring of molecule / diamond surface interactions.[19] The construction of the device is simple, cheap, and robust. Quartz microbalances operating at 5 MHz are capable of detecting changes in mass as low as 0.1 ng/cm^2, easily detecting most biomacromolecules. Hence, this device is an ideal biosensor for liquid or gas operation, with the added benefit of the wide electrochemical window of diamond.

[1] K. A. Marx, Biomacromolecules **4**, 1099 (2003).
[2] M. Rodahl, F. Hook, A. Krozer, P. Brzezinski, and B. Kasemo, Rev. Sci. Instrum. **66**, 3924 (1995).
[3] C. Eickes, J. Rosenmund, S. Wasle, K. Doblhofer, K. Wang, and K. G. Weil, Electrochim. Acta **45**, 3623 (2000).
[4] M. Hupert, A. Muck, R. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show, and G. M. Swain, Diamond Relat. Mater. **12**, 1940 (2003).
[5] Y. Kaibara, K. Sugata, M. Tachiki, H. Umezawa, and H. Kawarada, Diamond Relat. Mater. **12**, 560 (2003).
[6] A. Erdemir, C. Bindal, G. R. Fenske, C. Zuiker, A. R. Krauss, and D. M. Gruen, Diamond Relat. Mater. **5**, 923 (1996).
[7] Christian G. Specht, Oliver A. Williams, Richard B. Jackman, and Ralf Schoepfer, Biomaterials **25**, 4073 (2004).
[8] W. Yang, O. Auciello, J. E. Butler, W. Cai, J. A. Carlisle, J. Gerbi, D. M. Gruen, T. Knickerbocker, T. L. Lasseter, J. N. Russell, L. M. Smith, and R. J. Hamers, Nat. Mater. **1**, 253 (2002).
[9] W. L. Bragg and R. E. Gibbs, Proc. R. Soc. London, Ser. A **109**, 405 (1925).
[10] M. Daenen, O. A. Williams, J. D'Haen, K. Haenen, and M. Nesladek, Phys. Status Solidi A **203**, 3005 (2006).
[11] Y. R. Zhang, S. Asahina, S. Yoshihara, and T. Shirakashi, J. Electrochem. Soc. **149**, H179 (2002).
[12] I. A. Andreev, Tech. Phys. **49**, 1101 (2004); H. Fritze and H. L. Tuller, Appl. Phys. Lett. **78**, 976 (2001).
[13] D. Damjanovic, Curr. Opin. Solid State Mater. Sci. **3**, 469 (1998).
[14] O. A. Williams, M. Daenen, J. D'Haen, K. Haenen, J. Maes, V. V. Moshchalkov, M. Nesladek, and D. M. Gruen, Diamond Relat. Mater. **15**, 654 (2006).
[15] A. C. Ferrari and J. Robertson, Phys. Rev. B **63**, 121405 (2001).
[16] D. S. Knight and W. B. White, J. Mater. Res. **4**, 385 (1989).
[17] A. Hartl, E. Schmich, J. A. Garrido, J. Hernando, S. C. R. Catharino, S. Walter, P. Feulner, A. Kromka, D. Steinmuller, and M. Stutzmann, Nat. Mater. **3**, 736 (2004).
[18] J. M. Moon, S. Park, Y. K. Lee, G. S. Bang, Y. K. Hong, C. Park, and I. C. Jeon, J. Electroanal. Chem. **464**, 230 (1999).
[19] A. Alessandrini, M. A. Croce, R. Tiozzo, and P. Facci, Appl. Phys. Lett. **88**, 083905 (2006); F. Hook, J. Voros, M. Rodahl, R. Kurrat, P. Boni, J. J. Ramsden, M. Textor, N. D. Spencer, P. Tengvall, J. Gold, and B. Kasemo, Colloids Surf., B **24**, 155 (2002); M. Rodahl, F. Hook, C. Fredriksson, C. A. Keller, A. Krozer, P. Brzezinski, M. Voinova, and B. Kasemo, Faraday Discuss. **107**, 229 (1997); T. Zhou, K. A. Marx, M. Warren, H. Schulze, and S. J. Braunhut, Biotechnol. Prog. **16**, 268 (2000).