Thin Solid Films 619 (2016) 53–60

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Assessment of candidate metallization systems deposited on diamond using nano-indentation and nano-scratching tests

S. Msolli [a,*], J. Alexis [b], H.S. Kim [a], O. Dalverny [b], M. Karama [b]

[a] Department of Mechanical, Robotics and Energy Engineering, Dongguk University-Seoul, 30 Pildong-ro 1-gil, Jung-gu, Seoul 100-715, Republic of Korea
[b] Université de Toulouse, INP/ENIT, LGP, 47, Avenue d'Azereix, F-65013 Tarbes, France

ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form 28 September 2016
Accepted 8 October 2016
Available online 11 October 2016

Keywords:
Diamond
Metallization
Deposition
Nano-indentation
Nano-scratching
Power electronics

ABSTRACT

Mechanical suitability of ohmic contacts among the select metallization systems, deposited on a p-type heavily boron-doped homoepitaxial diamond layer, was evaluated via mechanical tests on the nanoscale. Two candidate metallization systems were considered: Si/Al and Ti/Pt/Au. Metallizations were performed using two different techniques: plasma-enhanced chemical vapour deposition and "lift-off". Effectiveness of the techniques was assessed via mechanical tests on the microscale and the nanoscale. Nano-indentation experiments were performed to determine the mechanical properties of the layers. Nano-scratching experiments were used to evaluate the mechanical adhesion on the diamond substrate. Scanning electron microscopy was applied for observation of the morphology of the surface and the indent and for detecting defects.

1. Introduction

Diamond is well known as a promising material for power electronics due to its desirable electrical and thermomechanical properties [1–3]. Nevertheless, many technological issues must be resolved to adequately exploit diamond and to manufacture competitive power electronic devices that can withstand high temperatures of up to 300 °C. This study focuses on diamond metallization systems that play the role of ohmic contacts. The metallization systems must satisfy many conditions, such as having the ability to withstand high voltages and current density, good mechanical properties, and good adhesion on the diamond substrate, among other requirements.

Many researchers are interested in the deposition of ohmic contacts on diamond based on the premise that good mechanical adhesion of the metallization systems is a key requirement for achieving efficient device bonding and power transmission. Refractory metals such as Ti, Mo, Ta, and W are known to form adhering carbide layers on diamond at high temperatures [4–6]. Ti-based contacts are more widely used due to the formation of a TiC layer during annealing, which enables achievement of low contact resistivity and good mechanical adhesion. Moreover, transition metals such as Cr, Ni, and Ni—Cr are widely used in other multi-chip module (MCM) technologies involving Si, *A*1N, SiC, and alumina substrates [7]. The mechanical and electrical performances of Cr, W, Ni, and Al layers as frameworks have been investigated and documented in the literature [8]. The ohmic contact metallization systems evaluated in the studies mentioned above were deposited on a diamond sample by the same photolithography process. It was noted that Ni is a suitable contact metallization system for utilization in high power, high temperature, and good mechanical strength diamond Schottky barrier diode applications. Nevertheless, the mechanical adhesion and thermal stability of these species was not investigated. The electrical capability and thermal stability after post-deposition annealing of metallization systems such as C/Ti/Ni, C/Ti/Cr, and C/Ti/W have previously been investigated. Under the relevant deposition conditions of these studies, it was concluded that the adhesion of Ti/Ni to diamond is higher than that of single layer Cu due to the formation of TiC, and that only Cr is inert to AuSn during annealing [9]. Cr also offers better adhesion and enhances the diffusion barrier properties (compared with Ti—W) for Au-based conductor metallization systems on diamond substrates [7]. From the latter observation, it can be deduced that both the die attachment and the diffusion mechanisms are highly important for the thermomechanical stability of the assembly involving diamond. The deposition technique also appeared to be of great importance. The adhesion of sputtered Au/(Ti—W) to diamond was significantly increased when the surface was activated by the sputter etch technique [7]. The electrical performance and intermetallic reaction of a Ti/Pt/Au multilayer after annealing at 800 °C and 900 °C under vacuum was also studied [10]. It was found that Au and Pt inter-diffused, but the Pt barrier was not fully consumed and effectively served as a barrier to Ti diffusion through the Au layer to the contact surface. Notably, some frameworks have been appended to Si/Al based contacts, leading to good electrical characteristics of such systems [11]. However, overall,

---

[*] Corresponding author.
E-mail address: sabeur.msolli@ensam.eu (S. Msolli).

http://dx.doi.org/10.1016/j.tsf.2016.10.022
0040-6090/

concrete advancements on the study of adhesion of such deposited films on diamond are rare.

Due to the lack of data concerning the mechanical and the adhesion characteristics of metallic films on diamond substrates, herein, we study some candidate metallization systems for use as ohmic contacts on diamond for high temperature power electronics. The ohmic contacts studied here are Ti/Pt/Au and Si/Al systems. The use of a thick Si or Ti layer allows the formation of a SiC or TiC carbide layer, which ensures strong bonding. This latter point is essential if high reliability of the diamond device packaging is required. Surface morphology analyses are performed using scanning electron microscopy (SEM) and the energy dispersive X-ray (EDX) technique to detect surface defects derived from deposition or annealing. Nano-indentation tests with large (XP) and small (DCM) displacements are performed to determine the elastic properties and hardness of the deposited films. Finally, the adhesion of the multilayers on the diamond substrate is evaluated using nano-scratching tests.

2. Experimental procedure

2.1. Deposition of thin films

*A*1.5 mm thick, heavily boron-doped diamond film deposited on the $3 \times 3 \times 0.5$ mm Ib. diamond sample used in this study. The boron density in the film was approximately 3×10^{20} cm^{-3}. The sheet resistance of the sample was measured by four probe measurement to be about 110 Ω/□. Various metallization systems were deposited on the diamond sample by vacuum evaporation. For Si/Al metallization, a 0.2 μm Si layer was first deposited at 475 °C by plasma-enhanced chemical vapour deposition (PECVD). The metallized substrate was then annealed in a rapid thermal processing (RTP) furnace at 1200 °C under vacuum for 10 s prior to cleaning with hydrofluoric acid to remove any oxides on the surface, including the native SiO_2. The purpose of this operation is to form a silicon carbide layer at the interface between silicon and diamond. This layer was used to help to ensure good adhesion of the layer stack on diamond. Upon completion of this operation, a 0.5 μm thick Al film was formed by the photolithography technique or by “lift-off”. This step was followed by annealing at 450 °C for 20 min in a tubular passage furnace to improve the adhesion of the metallization system.

On the second diamond substrate, a Ti/Pt/Au multilayer was formed by “lift-off”, where the multilayer comprised respective layers with thicknesses of 0.1, 0.05, and 0.5 μm. Once these films were obtained, the sample was annealed at 450 °C for 30 min. This is the minimum temperature at which Ti and Si form a carbide layer with diamond [11].

2.2. Mechanical characterization

2.2.1. Nano-indentation tests

The mechanical properties of the layers, such as the stiffness and hardness, were determined by using an MTS© nano-indentation device equipped with a Berkovich pyramidal indenter. This type of device can continuously measure the stiffness of the contact via “Continuous Stiffness Measurement”. Nano-indentation tests with small and large displacements were carried out at room temperature (23 °C) depending on the thickness of the deposited films. The test conditions are specified in Table 1. For large displacements, the tests were performed with an MTS XP nano-indenter in dynamic mode, making it possible to obtain the overall Hardness and Young's Modulus values of the multilayer. However, the DCM nano-indenter was utilized for small displacement (400 nm). The DCM nano-indenter permits determination of the individual properties of the films with quite good precision. The mechanical properties of the layers, such as the hardness and elastic modulus, were determined via the common Oliver-Pharr method [12]. For more details about the nano-indentation technique, one can refer to papers by Alexis or Msolli and co-workers [13–15], for instance.

Table 1
Operating conditions for nano-indentation tests.

Berkovich tip nature	DCM	XP
Load resolution	1 nN	100 nN
Column displacement resolution	0.05 nm	0.1 nm
Number of tests	30	10
Displacement into the surface	400 nm	2 μm
Approach velocity	8 nm/s	8 nm/s
Distance between nano-indents	10 μm	50 μm

2.2.2. Nano-scratching tests

The adhesion of the deposited multilayers was also assessed using nano-scratching tests. The test parameters were adapted depending on the thickness of the metallization layer (see Table 2). Nano-scratching tests were performed on the sample surface by moving a Berkovich tip in three successive steps and measuring the penetration depth. The first step was carried out to determine the surface topography and to correctly set the position of the indenter. The aim of the second step was to scratch the sample surface. The applied load was then increased progressively up to a maximal value and subsequently reduced. Finally, the spring-back and the topography of the residual scratch were measured from a last scan using a small applied load.

2.2.3. Morphology and EDX analysis

Observations were carried out with a field emission gun scanning electron microscope (FEG SEM-7000F from JEOL with the incident electron beam maintained between 10 and 15 kV) to analyse the surface morphology of the films. The analysis was corroborated by chemical analysis with an SDD Bruker X flash energy dispersive X-ray spectrometer (EDX).

3. Study of Si/Al metallization system

3.1. Morphology of the surface

Fig. 1 shows micrographs obtained by scanning electron microscopic (SEM) analysis of the metallization surface at various magnifications ranging from ×500 to ×50,000. The Si/Al multilayer did not have any detectable defects. The Si/Al multilayer appeared relatively dense and homogeneous at low magnification. Observations at higher magnification revealed the presence of clusters of a few microns, evenly distributed on the sample surface (Fig. 1a). The microstructure of the deposited Al comprised equiaxed grains with diameters of 100 nm (Fig. 1b).

EDX spot analyses were carried out on the metallization surface. The overall spectrum attests the presence of two layers of aluminium and silicon in region 3 (Fig. 1a). Indeed, the “interaction pear” of the SEM incident beam has a depth greater than the deposition thickness of aluminium, which also explains the detection of the sub-Si layer. However, the previously observed clusters denoted as region 4 (Fig. 1a) are those of aluminium because the Al content is higher than the Si content.

Table 2
Operating conditions for nano-scratching tests.

Distance between scratches	500 μm
Scratch length	700 μm
Scratching velocity	10 μm/s
Topography load	0.1 mN
Scratching load	0.1 mN to 80 mN
Final load	0.1 mN
Number of scratches	2 − 3