奈米平板鑽石成長及基材晶向對鑽石異質成核影響之研究

學生：陳厚光　　指導教授：張　立　博士

國立交通大學材料科學與工程學系博士班

摘要

本論文分成奈米平板鑽石及鑽石異質成核兩個主題來探討並敘述相關之結果。其中第一部分，將介紹一種具有獨特晶體形貌的二維度奈米結構鑽石及探討其成長機制。第二部分則是探討異質基材晶向對於鑽石在偏壓條件下成核的影響。

在第一部份中，利用高溫微波電漿化學氣相沉積法 (> 1100 ^{o}C) 可以分別在多晶、奈米晶粒鑽石基材及立方-八面體體鑽石晶粒上可以成長出大量二維奈米結構材料。透過一系列的穿透式電子顯微鏡的觀察及電子繞射跟電子能損能譜技術來鑑定其晶體結構及化學成分，證實這些二維奈米結構材料是單晶之立方鑽石晶體。整個奈米平板鑽石的平面平行於{111}晶面，外圍平板輪廓邊緣平行於<110>晶向，奈米平板鑽石厚度約 20~30 nm，邊長從 100 nm 至 2 μm 不等。

奈米平板鑽石會因為製程條件的改變，而呈現不同的形貌。在高甲烷濃度條件，多晶鑽石基材上成長的奈米平板鑽石，其外形結構是由各種形狀(近似於梯形及平行四邊形)的小平板組合而成，並且這些小平板會在平板鑽石表面形成平台及台階的結構。根據電子繞射及平板側向 TEM 觀察，奈米平板鑽石內部包含由許多跟平板平行的雙

晶。另外這些不同形狀的小平板也是以雙晶的方式彼此結合。在低甲烷濃度成長條件下，可以成長出規則六角形的單晶奈米平板鑽石。根據奈米平板鑽石在多晶鑽石基材及立方八面體鑽石晶粒上成長的觀察，平板鑽石只集中在鑽石基材{111}面上成長，並且會沿著鑽石基材<110>方向規則排列。論文中討論鑽石基材內部缺陷影響平板鑽石在鑽石基材上的排列及分佈的狀況。

利用高分辨率的穿透式電子顯微鏡觀察平板鑽石側面結構，發現平板鑽石側面是由{100}/{111}等晶面構成凸角結構，是非常罕見於一般平板雙晶體常見的{111}/{111}凹角結構。根據碳原子在這些晶面排列的原子模型加以推論，發現在雙晶平面跟{100}/{111}凸角結構交會點會產生次階梯結構。經由次階梯成長機制，使得鑽石以側向成長方式形成奈米平板之形狀。

在論文第二部分，探討異質基材晶向對於鑽石在偏壓條件下成核的影響。分別就在正負偏壓前處理下，鑽石在多晶 Ni_3Al 基材上成核行為進行研究。SEM 的觀察發現鑽石不論是透過正或是負偏壓，在不同晶向晶粒上呈現不同的成核密度。針對正偏壓的試片，利用電子背向散射繞射(EBSD)分析技術，針對不同晶向的晶粒及所對應鑽石成核密度進行一系列的觀察及統計。發現鑽石在同一個試片中，在{111}晶面的晶粒上有最高的鑽石成核密度。然而在{110}及{100}則成核密度非常低。論文中將討論 Ni_3Al 表面結構對鑽石成核的影響。另外，將透過橫截面 TEM 的觀察來分析兩種不同成核偏壓前處理的試片的介面結構，發現在經過正偏壓前處理的試片，鑽石跟 Ni_3Al 基材介面非常平整；然而在負偏壓的試片，鑽石跟 Ni_3Al 基材介面非常粗造，並且有許多 Ni_3Al 奈米顆粒散佈在 Ni_3Al 基材表面上。

The Growth of Diamond Nano-platelets and Substrate Orientation Effect on Diamond Heterogeneous Nucleation

student：Hou-Guang Chen　　Advisors：Dr. Li Chang

Abstract

The dissertation is divided into two parts. In the first part, we demonstrate growth of a two-dimensional nano-structured diamond in a unique platelet morphology which differs from the usual habit of diamond growing under conventional chemical vapor deposition (CVD) condition. The growth mechanism of the diamond nano-platelets was studied by the electron microscopy. In the second part, we investigate the effect of substrate orientations on diamond heterogeneous nucleation with bias enhanced pretreatment.

In the first part of the dissertation, it is shown that a large quantity of a two dimensional nano-structured materials can grow on polycrystalline, nanocrystalline and isolated cubo-octahedral diamond substrates by high temperature microwave plasma CVD. According to the characterization of electron microscopy, these platelet-like nano-materials are identified as single crystalline cubic diamond crystallite. The tabular surfaces of the diamond platelets are parallel to diamond {111} plane, and the edges of the platelets are along the [110] direction. The diamond nano-pletelets have a thickness of about 20~30 nm.

The morphology of the diamond nanoplatelets varies with the growth conditions. In the case of growth on the ploycrystalline diamond substrates under high methane concentration condition, diamond nano-platelets consisting of many smaller tabular crystallites with various shapes but with the same facets, such as trapezoid and parallelogram, appear in terrace and step structure on tabular surface. Based on transmission electron microscopy (TEM) observation in side-view direction, the diamond nano-platelets contain multi-parallel twins parallel to the {111} tabular plane of the platelets. Indeed, these small tabular crystallites compose diamond nano-platelets in twins. In the case of growth under low methane concentration condition, single-crystalline diamond nano-platelets in shape of regular hexagon can be obtained. According to the growth of diamond nano-platelet on polycrystalline diamond substrate or on isolated cubo-octahedral diamond particles, diamond nano-platelets only grow on {111} facets on diamond substrates, and arrange in an array along <110> directions of diamond. The arrangement and distribution of diamond nanoplatelet on diamond substrate depends closely upon the distribution of defect in diamond substrate.

High-resolution transmission electron microscopy demonstrates the first observation in diamond structure that the side-face structure of diamond nano-platelets appears in ridge edge structure bounded by {100}/{111} facets, instead of the {111}/{111} re-entrant groove

structure which emerges from tabular twinned crystallite usually observed in CVD diamond growth. According to atomic model with respect to arrangement of carbon atoms on crystal facets, it is understood the reason why the {100}/{111} ridge with a sub-step emerged from twins acts as a self-perpetuating source for lateral growth resulting in platelet shape.

In the second part of the dissertation, we show the effect of the grains in different crystallographic orientations on diamond heterogeneous nucleation with bias enhanced pretreatment. Diamond deposition with positive and negative bias enhanced nucleation pretreatments on mirror polished polycrystalline Ni_3Al substrates has been investigated, respectively. According to scanning electron microscopy (SEM) observation, it was found that diamond deposition on the substrates under both biasing applications exhibited significant variations among grains of different orientations. Thus, the correlation of the crystallographic orientation of grains on the samples with the diamond nucleation behavior was systematically characterized for the case of positive biasing by electron backscattered diffraction method with scanning electron microscopy. Diamond deposition on Ni_3Al grains near {111} orientation results in higher nucleation densities, while the densities are low on {110} and {100} oriented grains. The effect of the Ni_3Al surface structure on diamond nucleation has been discussed. Also, the interfacial microstructure between diamond deposited and Ni_3Al was characterized by cross-sectional transmission electron microscopy. The interfacial

structure between diamond and Ni_3Al was smooth in the case of positive biasing. However, negative bias pretreatment resulted in surface roughening of Ni_3Al substrate and forming a large number of Ni_3Al nano-particles.