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Growth of epitaxial diamond on silicon via iridium/$SrTiO_3$ buffer layers

T. Bauer[a], S. Gsell[a], M. Schreck[a,*], J. Goldfuß[a], J. Lettieri[b], D.G. Schlom[b], B. Stritzker[a]

[a]*Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany*
[b]*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802-5005, USA*

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Abstract

Large-area, single-crystalline iridium films are desired for the heteroepitaxial deposition of diamond. In the present work, we studied the potential of $SrTiO_3$ buffer layers for the epitaxial deposition of iridium on silicon. Molecular beam epitaxy (MBE) was used to deposit a 100-nm-thick $SrTiO_3$ layer. On top of this, iridium films were grown by e-beam evaporation. Subsequently, diamond was nucleated by the bias-enhanced nucleation procedure. The epitaxial orientation relationship of the resulting multilayer structure is diamond(001)[110] ||Ir(001)[110]||$SrTiO_3$(001)[110]||Si(001)[100]. The Ir/$SrTiO_3$ buffer layers lower the misorientation of the epitaxial diamond films by nearly an order of magnitude as compared to deposition directly on silicon. Oxides like yttria-stabilized zirconia (YSZ) or CeO_2/YSZ prepared by pulsed laser deposition (PLD) provide a viable alternative to the MBE-grown $SrTiO_3$. The crystalline quality of the diamond films and their good adhesion on the silicon substrate suggest diamond/Ir/metal-oxide/Si as a promising means to a large-area, single-crystal diamond technology.

Keywords: Diamond growth and characterization; Heteroepitaxy; Bias-enhanced nucleation; Iridium

1. Introduction

High-quality diamond material with excellent electronic properties can be produced with chemical vapor deposition (CVD) methods by growing homoepitaxial layers on Ib-type high-pressure, high-temperature (HPHT) substrate crystals [1]. Unfortunately, due to the limited size of available HPHT samples, this concept can currently not fulfill the requirements with respect to sample size for a future diamond technology. In the related field of heteroepitaxy, there has been a protracted search for an appropriate substrate material. Since the first studies of diamond nucleation on iridium, this noble metal has established itself as a unique material for the formation of heteroepitaxial diamond [2,3]. Thus, finding an appropriate substrate for the epitaxial overgrowth of iridium is now a major challenge in this field.

Single-crystal metal films can be grown on a variety of oxide crystals like Al_2O_3 [4], $SrTiO_3$ [3], and MgO [2]. All these substrates have successfully been employed for the epitaxial growth of iridium, upon which diamond has been grown epitaxially. It turned out, however, that adhesion of the diamond layers is a severe problem. This results from the huge misfit in thermal expansion coefficients. We calculated the thermal stress developing after cooldown from a deposition temperature of 700 °C assuming a thin diamond film with an iridium buffer layer on top of a thick substrate crystal. The obtained compressive stress values were −4.05, −6.44, and −8.3 GPa for Al_2O_3, $SrTiO_3$, and MgO, respectively [5]. Compared with these oxides, silicon with only −0.68 GPa represents a much better solution.

In a recent publication, we have shown that yttria-stabilized zirconia (YSZ) buffer layers grown by pulsed laser deposition (PLD) facilitate the growth of epitaxial iridium films on silicon [5]. Thick, high-quality diamond layers with good adhesion were formed using the multilayer

* Corresponding author. Tel.: +49 821 598 3401; fax: +49 821 598 3425.
E-mail address: matthias.schreck@physik.uni-augsburg.de (M. Schreck).

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structure diamond/Ir/YSZ/Si(001). After this proof of concept, it is now necessary to find the optimal oxide whose preparation can be easily scaled up and which allows the highest structural quality of epitaxial iridium layers. In the present work, we have studied $SrTiO_3$ layers prepared by molecular beam epitaxy (MBE) as an alternative to YSZ buffer layers.

2. Experimental

A 100-nm-thick heteroepitaxial $SrTiO_3$ layer was grown on a 2-in. Si(001) wafer by MBE at Penn State University. A detailed description of the growth is given elsewhere [6]. In brief, after reacting a half monolayer of strontium metal at ~700 °C with a thermally cleaned and 2×1 reconstructed surface of Si(001) to form a thin epitaxial strontium silicide layer, two monolayers of epitaxial SrO were grown epitaxially at a substrate temperature of ~100 °C in an oxygen background pressure of 2×10^{-8} Torr [7]. This was followed by the deposition of one monolayer of amorphous TiO_2 at an oxygen background pressure of 5×10^{-8} Torr, also at ~100 °C. The oxygen was turned off and the sample was then slowly heated to about 500–550 °C until the TiO_2 diffused into the SrO bilayer forming $SrTiO_3$ via a topotactic reaction. With the substrate at 500–550 °C, oxygen was again introduced at a background pressure of 1×10^{-8} Torr and additional $SrTiO_3$ was epitaxially grown by depositing alternating monolayers of TiO_2 and SrO by shuttering the titanium and strontium molecular beams to provide monolayer doses to the growing surface [8].

This sample was then cut into 1×1 cm^2 pieces before 150-nm-thick iridium layers were deposited by e-beam evaporation at a substrate temperature of 650 °C. This temperature is significantly lower than the 900–950 °C used in former experiments for growth on $SrTiO_3$ single-crystal substrates for two reasons: (1) We tried to avoid a reaction and further oxidation at the interface between $SrTiO_3$ and Si. (2) A slight compressive stress in the iridium layer under diamond deposition conditions is preferable. For silicon as the bulk substrate, this requires an iridium deposition temperature below the diamond growth temperature of 700 °C.

Diamond growth was performed in a microwave plasma CVD setup in a gas atmosphere of CH_4 in H_2 at 700 °C. Gas pressure and microwave power were 30 mbar and 1100 W, respectively. Epitaxial nucleation was induced by the BEN procedure applying a bias voltage of about −280 V for 60 min. The CH_4 content of 7% in the BEN step was reduced to 1% in the subsequent growth process. During the whole process, 40 ppm N_2 was added to the gas phase. The growth rate was typically 0.5–1 μm/h.

X-ray diffraction (XRD) characterization of the samples was carried out using a Siemens D5000 for pole figure and mosaicity measurements and a Seifert XRD 3003 PTS-HR high resolution diffractometer with parallel beam geometry. The latter was operated either in the high resolution mode in which a Bartels-type Ge(220) monochromator provides pure $CuK_{\alpha1}$ radiation or in a mode in which the parallel beam was only formed by a graded parabolic X-ray mirror.

3. Results

Fig. 1 shows an X-ray diffractogram of the $SrTiO_3$ layer on Si(001) in a semi-logarithmic plot. Only peaks of the (00 h) family of reflections are visible, which proves the excellent epitaxial quality of the MBE-grown oxide film. From rocking curves, a full width at half maximum (FWHM) of 0.57° was deduced for the tilt. From azimuthal scans of the $SrTiO_3$(101) Bragg reflex, the epitaxial orientation relationship $SrTiO_3(001)[110]\|Si(001)[100]$ was determined. The 45° rotation of the $SrTiO_3$ unit cell with respect to the silicon lattice enables a good lattice fit between $a(SrTiO_3)=0.3905$ nm and $1/\sqrt{2}a(Si)=0.384$ nm. The FWHM of the azimuthal scan was 1.3°.

Fig. 2 shows a θ–2θ scan of a 150-nm-thick iridium layer grown on top of the $SrTiO_3$/Si(001) sample. As compared to the dominant Ir(002) peak, the (111) texture component is weaker by three orders of magnitude. For the subsequent epitaxial diamond growth, this small contribution is of negligible relevance.

After the BEN step, the diamond films were grown for a short time so that the epitaxial quality of the layer could be easily checked by scanning electron microscopy (SEM). Fig. 3 shows two samples "A" and "B" after 60 min bias and 60 or 30 min growth, respectively. On sample "A", a high density of oriented diamond crystallites is visible. In contrast, on "B" the crystallites have already merged to from a homogeneous flat surface with few interstices. The low density of these aligned interstices indicates the good epitaxial orientation of the film. We suppose that during the growth of sample "B" the substrate temperature was slightly higher due to a worse

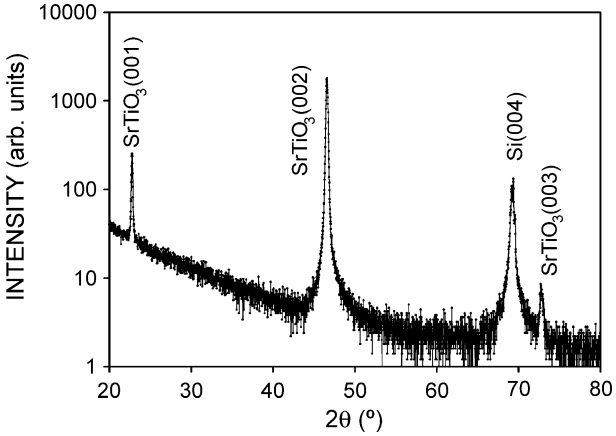

Fig. 1. θ-2θ-scan of a 100-nm thick $SrTiO_3$ layer on Si(001) grown by MBE.

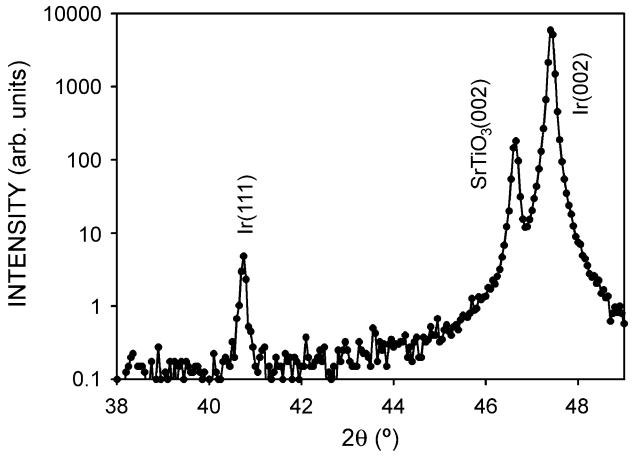

Fig. 2. θ-2θ-scan after deposition of 150 nm Ir on the $SrTiO_3$/Si(001) sample.

thermal contact with the substrate holder. As known from former experiments, a temperature increase by only 10–20 °C can be sufficient to modify the texturing significantly by enhancing the lateral growth mode.

XRD pole figures were measured to characterize the texture and determine the orientation relationships. Fig. 4 shows the direct comparison between the pole figures for (a) Si{111}, (b) $SrTiO_3${101}, (c) Ir{111}, and (d) Dia{111} reflections of sample "A". All pole figures are dominated by one single-texture component. The orientation relationship of the present multilayer structure is: diamond(001)[110] ||Ir(001)[110]||$SrTiO_3$(001)[110]||Si(001)[100]. Diamond (004) rocking curves and diamond (311) azimuthal scans were measured for the two samples in Fig. 3. Their FWHMs are 1.3° ("A") and 1.04° ("B") for the polar and 1.7° ("A") and 1.94° ("B") for the azimuthal scan. These values have to be compared with typically 1° measured in former experiments for thin diamond films on Ir/$SrTiO_3$(001) [9].

By extending the duration of the growth step, the texture could be strongly improved. Fig. 5 shows a rocking curve and an azimuthal scan of a diamond film with a thickness of 16.5 μm. Both FWHMs were significantly reduced to 0.38° and 0.98°, respectively.

Fig. 6(a) and (b) shows optical and SEM images of the thick sample. It is homogenous and flat over the whole

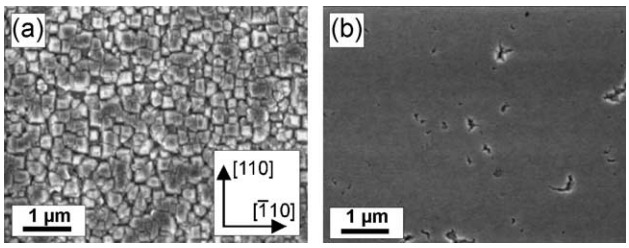

Fig. 3. Scanning electron micrographs of two diamond films grown on Ir/$SrTiO_3$/Si(001) substrates. a) Sample "A": 60 min bias and 60 min growth. b) Sample "B": 60 min bias and 30 min growth at slightly higher temperature.

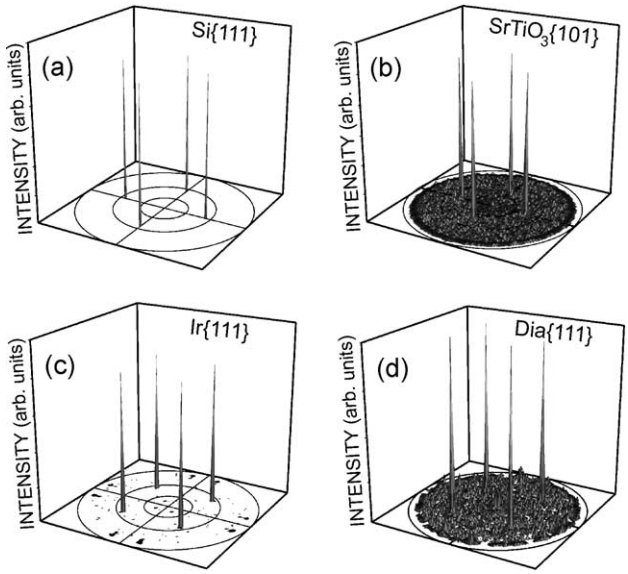

Fig. 4. X-ray pole figures of sample "A" (linear intensity scale).

diameter of the sample which can be recognized from the reflection of the calliper rule in Fig. 6(a).

4. Discussion

The present results show that epitaxial iridium films which are the key component for heteroepitaxial diamond growth can successfully be deposited on silicon single crystals by using $SrTiO_3$ buffer layers. These buffer layers transfer the information about the substrate crystal orientation and apparently suppress any chemical reaction between silicon and iridium. They sustained the harsh CVD environment during diamond nucleation and growth. Future experiments have to show whether they are also stable under high growth rate process conditions for a longer process time.

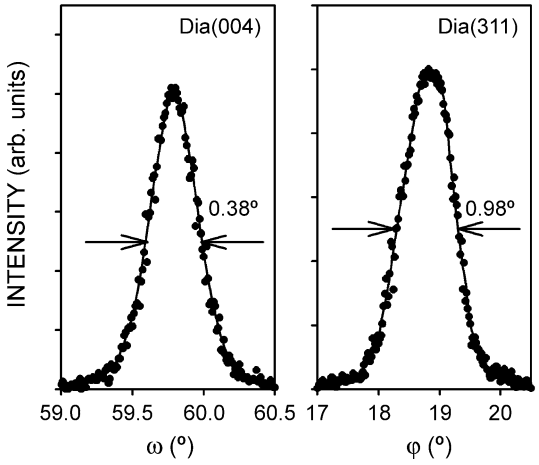

Fig. 5. Diamond (004) rocking curve and diamond (311) azimuthal scan of a 16.5 μm thick heteroepitaxial diamond film on Ir/$SrTiO_3$/Si(001). The data were fitted by Gaussian curves.

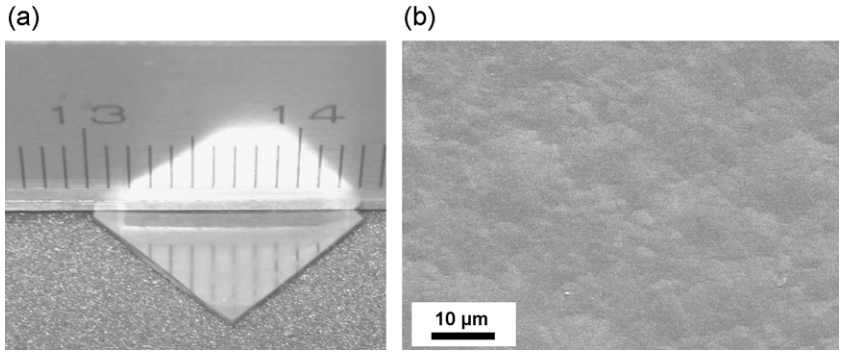

Fig. 6. (a) Optical image and (b) scanning electron micrograph of the thick diamond layer (substrate size 1 cm×1 cm).

The mosaicity of the thin diamond films nucleated on the Ir/$SrTiO_3$/Si(001) samples is only slightly higher than for films of comparable thickness grown on Ir/$SrTiO_3$(001). The subsequent textured growth step improved tilt as well as twist concurrently. The underlying mechanisms for this phenomenon have recently been studied and described in Ref. [10]. Comparing the two samples of Fig. 3, it is noteworthy that the lower value for the tilt of sample "B" is accompanied by a higher twist. This observation conclusively fits to the assumption that in the smoother layer "B" texture improvement was mainly induced by the lateral flow process. Further data are required to corroborate this result, which would strongly support our considerations concerning a targeted texture improvement [10].

With absolute values for tilt and twist of the thick film below 1°, the present samples are by a factor of 5 better than diamond grown directly on silicon. They exceed heteroepitaxial diamond layers on any other substrate which does not contain iridium. Thus, the multilayer structure diamond/Ir/$SrTiO_3$/Si(001) represents a promising concept for the realization of large-area diamond wafers.

Recently, we have shown that YSZ buffer layers can be used to grow iridium and diamond on silicon. These YSZ layers had been prepared by PLD. The present $SrTiO_3$ buffer layers prepared by the MBE technique represent a viable alternative. In further experiments, we have also synthesized modified buffer layer systems like CeO_2/YSZ/Si(001) and $SrTiO_3$/CeO_2/YSZ/Si(001) by PLD. It turned out that these also facilitate the growth of epitaxial iridium films on silicon. Without having explicitly done the corresponding experiments, we expect that they will also allow the epitaxial deposition of diamond.

5. Summary and conclusions

In this work, we have presented MBE-grown $SrTiO_3$ as a new material which can serve as an efficient buffer layer for the epitaxial growth of iridium and thereupon of diamond on silicon. Considering further experiments with YSZ, CeO_2/YSZ and $SrTiO_3$/CeO_2/YSZ, we conclude that oxide films apparently overcome the drawbacks of other buffer layers like CaF_2 [11] and provide a promising route for the future realization of large-area, single-crystal diamond wafers.

Besides the proof of concept, our experiments point out different solutions for the choice and preparation method of appropriate epitaxial oxides on silicon. Future work has to clarify which buffer layer facilitates the highest quality diamond layers on silicon. Thereby, beyond the aspect of epitaxy, technical issues like the ease of upscaling and the stability of the different interfaces (adhesion) will play a decisive role.

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