Applications of Diamond Films and Related Materials
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CHARACTERIZATION OF TITANIUM SILICIDE CONTACTS DEPOSITED ON SEMICONDUCTING DIAMOND SUBSTRATES

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Abstract

The first results pertaining to the growth and characterization of titanium silicide contacts deposited on natural semiconducting diamond substrates are reported. The titanium silicide films were formed by the co-deposition of silicon and titanium in ultra-high vacuum by electron-beam evaporation in a molecular beam epitaxy (MBE) system. The grown layers have been characterized using Raman spectroscopy, scanning tunneling microscopy (STM) and current-voltage (I-V) techniques. In particular, it has been shown from I-V measurements taken at room temperature that the titanium silicide film forms a low-barrier rectifying contact. Consistent with the observed low-barrier height, the corresponding I-V measurements recorded at 400°C exhibit ohmic-like behavior. However, on subsequent annealing of the titanium silicide contacts at 1100°C, stable rectifying I-V characteristics were observed in the 25 - 400°C temperature range.

1. INTRODUCTION

Diamond affords the potential as a future material system for the development of high temperature, high power and high frequency electronic device applications [1]. In particular, it is evident that the fabrication of metal contacts to diamond will play an important role in the realization of these diamond-based device technologies. At present there is a significant scientific and technological interest in achieving stable high-temperature ohmic and rectifying contacts to semiconducting diamond. For instance, recent studies have shown both ohmic and Schottky behavior for a wide range of metal and metal/alloy contacts to both CVD grown diamond thin films and natural semiconducting diamond substrates [2-7]. In addition, the refractory metal silicides such as those of Ti and Mo have been proposed as alternative contact materials to diamond and are currently being investigated in our laboratory. Indeed, it is interesting to note that the metal silicides are widely used in silicon IC technologies as low-resistivity source/drain contacts in MOS device structures [8].

In this study we present the first results pertaining to the optical, microstructural and electrical characterization of titanium silicide films deposited on natural semiconducting diamond substrates.

2. EXPERIMENTAL PROCEDURE

Several commercially supplied (D. Drukker & ZN.N.V.) low resistivity (~10^3-10^4 Ω-cm, p-type) natural diamond (surface orientation (001)) substrates were chemically cleaned in a mixture of $1H_2SO_4$:$1H_2O_2$ for 10 min followed by a deionized water rinse and dried using filtered N_2. Following cleaning, the samples were mounted on a molybdenum sample holder and transferred into the molecular beam epitaxy (MBE) system. Prior to deposition, the diamond substrates were annealed to 800°C for 10 mins to thermally desorb both water vapor and possibly physi-adsorbed gas contaminants. The substrate temperature was then lowered to 550°C and a titanium silicide film was grown by the co-deposition of titanium and silicon using electron-beam evaporation. By employing a stainless steel contact mask several titanium silicide dots of ~50 nm thickness and 3 x 10^{-3} cm^2 in area were fabricated. The corresponding deposition rates for titanium and silicon were typically 12 nm/min and 24 nm/min, respectively. The pressure in the MBE chamber during deposition was typically better than 9 x 10^{-9} Torr. Subsequent annealing of the samples was preformed at a temperature of 1100°C at 10^{-6} Torr for 30 min in a quartz furnace.

The as-deposited and annealed titanium silicide films were characterized using Raman spectroscopy, STM and I-V measurement techniques.

3. RESULTS AND DISCUSSION

Raman scattering spectroscopy analysis of the grown layers has identified the metastable orthorhombic C49 crystal structure of $TiSi_2$. Shown in Figure 1 is the corresponding Raman spectrum obtained at room temperature using an Ar^+ ion laser (514.5 nm) excitation source. The spectral features pertaining to both $TiSi_2$ and single-crystal Si are clearly evident [9]. It is apparent that the presence of the Si LO phonon peak at 520 cm^{-1} is indicative of excess Si incorporation during growth.

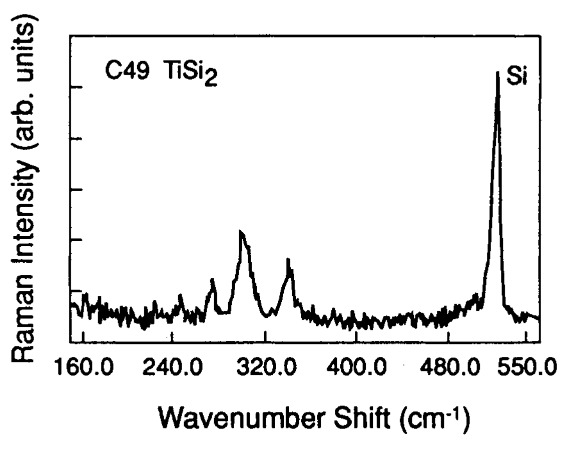

Figure 1. Raman spectrum of the metastable C49 phase of $TiSi_2$ deposited on semiconducting diamond.

As evidenced by STM the $TiSi_2$ films exhibit a textured and faceted surface morphology indicative of polycrystalline growth. Figure 2 shows the STM micrograph of the as-deposited $TiSi_2$ layers. The corresponding surface roughness has been determined to be

~ 23 nm (peak to peak).

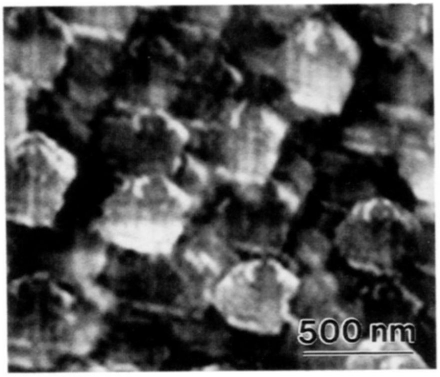

Figure 2. Topographic (constant current) STM micrograph of the surface morphology of $TiSi_2$ films deposited on semiconducting diamond.

A sheet resistivity (R_s) of ~10 $\Omega/\square$ was determined from four-point probe measurements [10]. Current-voltage (I-V) measurements were obtained using a HP 4145A semiconductor parameter analyzer. The diamond substrates were mounted on a copper plate using silver paint to form a large area back contact. Sample heating in the temperature range between 25-600°C was achieved using a ceramic heater assembly. Current-voltage measurements were obtained by grounding the copper plate and applying a bias to the $TiSi_2$ contact using a tungsten probe. Shown in Figure 3 are the room temperature I-V characteristics obtained for the as-deposited $TiSi_2$ contacts.

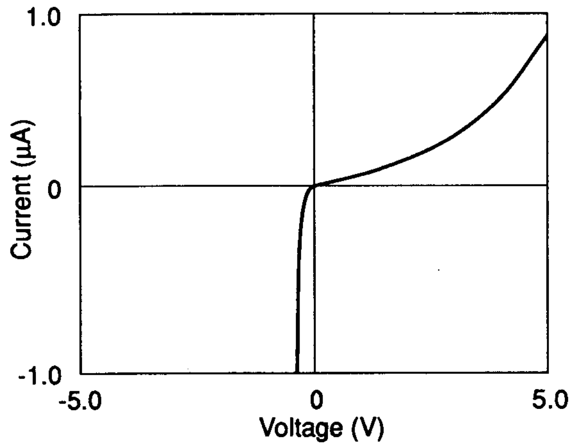

Figure 3. I-V characteristics of $TiSi_2$ contacts on semiconducting diamond at 25°C.

The rectifying character of the as-deposited $TiSi_2$ films is clearly evident. In particular, the observed forward bias turn-on voltage was ~0.2 V with a reverse bias leakage current of ~800 nA at 5 V. Consistent with the observed low-barrier height (small turn-on voltage), the corresponding I-V measurements recorded at 400°C exhibit ohmic-like behavior. However, on subsequent high-temperature annealing at 1100°C for 30 min at 10^{-6} Torr, stable rectifying I-V characteristics were observed at both room temperature and 400°C. Moreover, it was apparent from Raman spectroscopy measurements that the surface of the natural diamond substrate had graphitized following the annealing process. Indeed, it has been shown that the presence of the graphitic sp^2 layer contributes to the measured reverse bias leakage current [11]. Consequently, prior to electrical characterization it was necessary to remove the non-diamond carbon using a CrO_3:H_2SO_4 cleaning procedure. Shown in Figures 4 and 5 are the corresponding I-V characteristics for the chemically cleaned high-temperature annealed $TiSi_2$ contacts recorded at room temperature and 400°C, respectively.

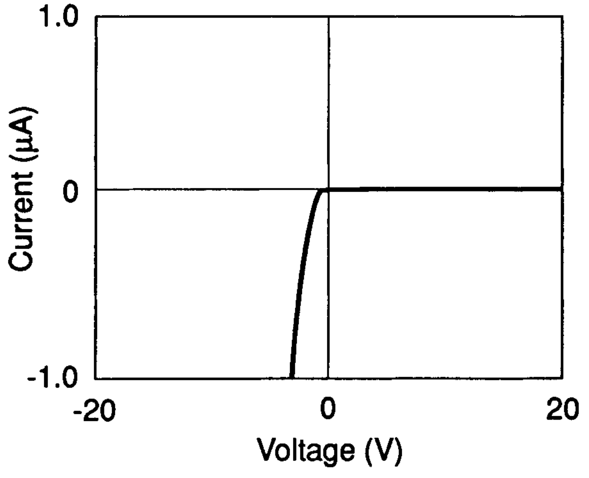

Figure 4. I-V characteristics of the chemically cleaned high-temperature annealed $TiSi_2$ contacts at 25°C.

It is apparent that the rectifying behavior of the annealed $TiSi_2$ contacts has been upgraded. In particular, at room temperature a relatively small leakage current of ~4 nA was observed at a reverse bias of 20 V. However, upon heating to 400°C the leakage current increased to ~400 μA which is equivalent to 0.13 A/cm^2. Indeed, these contacts appear to be very stable at this measurement temperature without any apparent degradation. As a consequence of interface chemical reactions the annealed $TiSi_2$ contacts exhibit excellent adhesion properties with the underlying diamond substrate. For instance, it has been observed that the mechanical adherence of the contacts does not degrade following various processing (ultrasonic cleaning, thermal cycling and electrical probing) steps. In contrast, metal films deposited at room temperature, for example Au, have a tendency to peel from the diamond surface during processing [12].

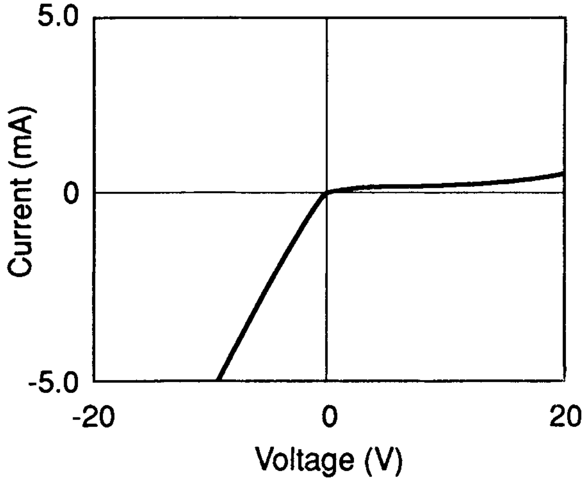

Figure 5. I-V characteristics of the chemically cleaned high-temperature annealed $TiSi_2$ contacts at 400°C.

3. CONCLUSION

In summary, $TiSi_2$ films have been deposited on semiconducting diamond substrates. The grown layers have a textured and faceted surface topography indicative of polycrystalline growth. Corresponding I-V measurements of the as-deposited $TiSi_2$ contacts has demonstrated rectifying characteristics at room temperature. However, subsequent post-growth annealing of the films at 1100°C has significantly upgraded the electrical transport properties such that stable high-temperature rectifying contacts can be achieved in the 25-400°C temperature range.

4. ACKNOWLEDGEMENTS

The authors wish to thank Professor R.F. Davis (NCSU) for many helpful discussions. TPH, HJ, KFT, JVL and RJN gratefully acknowledge partial support from the National Science Foundation (Contract No. DMR-8717816). JBP gratefully acknowledges support from the Strategic Defense Initiative Organization / Innovative Science and Technology through the Office of Naval Research (Contract No. N00014-86-C-0460).

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