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Journal
Review of Scientific Instruments, 88(4)

ISSN
0034-6748

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Publication Date
2017-04-01

DOI
10.1063/1.4980149

Peer reviewed

Published in

Rev. Sci. Instrum. **88** (2017) 043506.

http://dx.doi.org/10.1063/1.4980149

Sputtering of pure boron using a magnetron without a radio-frequency supply

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Manuscript of 2017-04-03

ACKNOWLEDGMENTS

The work is supported by Russian Science Foundation under grant # 16-19-10034. Work at LBNL is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Abstract

Boron at room temperature is insulating and therefore conventionally sputtered using radio-frequency (RF) power supplies including their power-matching networks. In this contribution we show that through a suitable ignition assistance, via temporary application of a high voltage (~ 600 V) to the substrate holder or auxiliary electrode, the magnetron discharge can be ignited using a conventional mid-frequency power supply without matching network. Once the discharge is ignited, the assisting voltage can be reduced to less than 50 V, and after the boron target surface is at elevated temperature, thereby exhibiting sufficient conductivity, the assisting voltage can be turned off. The deposition of boron and boron nitride films has been demonstrated with a deposition rate of approximately 400 nm/h for a power of 250 W.

I. INTRODUCTION

Boron is widely used in ion implantation and thin film applications. For example, boron ions are used for ion-beam doping of semiconductors,[1] for surface modification by ion implantation,[2,3] for synthesizing boron-containing films and coatings such as boron nitride,[4] and for trench filling in particle detectors.[5] Boron-based coatings can significantly improve the surface properties of the materials for diverse applications since the coatings exhibit high hardness, toughness, corrosion resistance, and wear resistance, and extreme case rival properties of diamond.[6] For all these reasons, being able to sputter boron is highly relevant, and for many application especially interesting when a conventional planar magnetron can be used[7].

The most common method of producing boron-containing coatings with a planar magnetron is to use a target of a boron-containing compound, where the non-boron component is used to directly obtain the desired boron compound film, and/or utilize the target's electrical conductivity that comes with the addition of the component. Among the most-often used boron-containing targets are BN (ref.[8,9]), B_4C (ref.[10]), $AlMgB_{14}$ (ref.[11]), FeB, TiB_2, CrB_2 (ref.[12,13]), as well as some hexaborides such asLaB_6, CeB_6, SmB_6, YB_6 (ref.[14-16]).

Magnetron targets made of pure boron have been mainly used in semiconductor doping technology[17] as well as to deposit boron nitride films by reactive magnetron sputtering, when the pure boron target operates in a nitrogen atmosphere.[18] However, pure boron has very low electrical conductivity. As for any other dielectric targets, this leads to a host of issues including charge-up of the target surface followed by increased arcing. Another problem is covering of the anode by a non-conductive film, blocking the flow of electrons from the plasma, often resulting in discharge instabilities and stopping the discharge altogether, an effect known as the "disappearing anode problem."[19,20]

To sputter dielectric (insulating) targets, sputtering magnetrons usually operate at radio-frequency (RF) at the standard frequency of 13.56 MHz, ref.[7,21,22] Other frequencies are possible but the system needs to be very well-shielded to avoid illegal radio interference. RF magnetrons can be used produce films of boron (and other materials) of high purity, with applications e.g. in the field of microelectronics. However, RF sputtering has significant disadvantages compared to other forms of sputtering, including a low deposition rate (typically less than 1/2 of the dc magnetron sputtering rate), a low power efficiency, high cost, and constraints in terms of scaling to large surface areas.[7,21,22]

The development of high-power semiconductor switches allowed the fabrication of power supplies for pulsed magnetrons operating in mid-frequency range of 10-100 kHz, and in some cases up 350 kHz.[7,23-25] This has the advantage that arcing processes are reduced to a level that arcing do not significantly affect the quality of the sputter-deposition process.[7,19] Power supplies with asymmetric bi-polar voltage and current pulse shapes are designed to sputter targets at negative pulse polarity and remove accumulated surface charge by allowing plasma electrons to arrive on the surface during positive polarity phase of the pulse cycle. This is relevant for poorly conducting targets, or targets with a dielectric layer (a.k.a. “poisoned” targets).

Using RF sputtering, planar magnetrons are able to operate with any dielectric targets but practically no literature is available describing the use of planar magnetrons with pure boron targets other than RF-sputtering. Magnetron operation with a pure boron target at relatively low frequency (low compared to RF) might avoid the drawbacks associated with RF magnetrons. Thus, the goal of the present study is precisely to explore the possible functioning of magnetron in the mid-frequency range when using a target of pure boron.

II. EXPERIMENTAL SETUP

A schematic view of the experimental setup is shown in Fig.1. A water-cooled, planar magnetron with a 50 mm (2 inch) target was mounted in a large, stainless steel vacuum chamber of 1 m inner diameter and 25 cm inner height, which was cryogenically pumped (CryoTorr 1500 l/s). The target was made from boron (purity 99.5%). In initial experiments, in order to test and assess the system’s operational properties, a silicon target (purity99.999%) was also used. The magnetron, with a grounded anode, operated in the mid-frequency pulsed mode fed by a Pinnacle®Plus (Advanced Energy) power supply. This power supply delivers asymmetric, bi-polar, rectangular pulses with a power up to 5 kW and a pulse frequency up to 350 kHz. After each negative pulse (voltage up to -650 V), a slightly positive (”reverse”) pulse can be set; we chose a duration of0.6 µs. In most experiments, except when studying the current-voltage characteristic of the magnetron discharge, we used the

Pinnacle®Plus in constant power mode with the (time-averaged) power set in the range from 150 W to350 W.

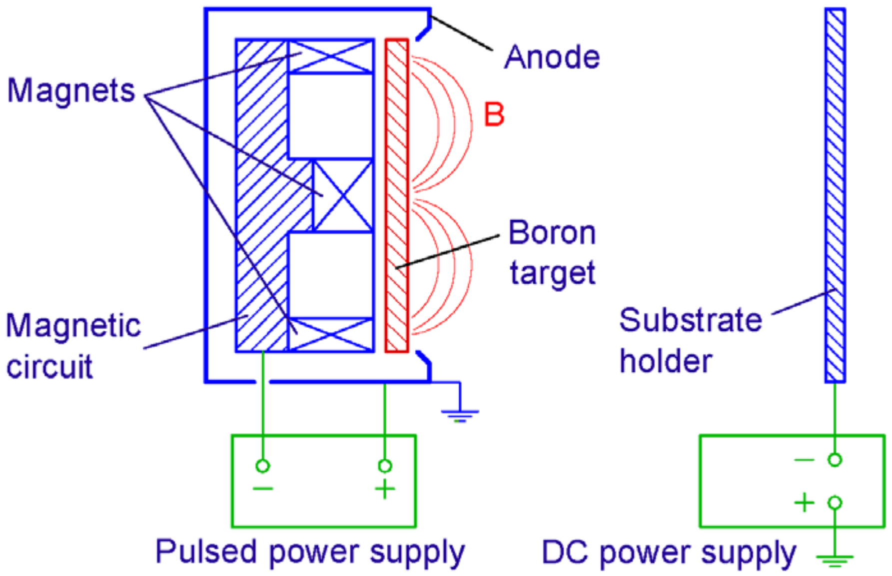

Fig. 1. Experimental setup

A flat substrate holder, made from metal but mounted in an electrically insulated manner, was located 7 cm from the magnetron target. Initially it was installed to hold samples to deposit boron or boron-containing films. However, during the experiments it became clear that the presence of this holder has an influence on the ignition of the magnetron discharge when using a boron target. Therefore, the holder was negatively biased to different voltages with respect to ground using a Glassman dc power supply (maximum voltage 1 kV, maximum current 3A).

Most of the experiments were carried out with nitrogen as operating gas motivated by the general interest inefficient deposition of boron nitride films, though the focus of the current research was on the ability to ignite plasma and less to deposit and study films. Pure argon, oxygen, and mixtures of gases were also used in experiments. Gas flow rates were regulated with mass flow controllers (MKS) and the pumping speed between chamber and the cryogenic pump could be selected via an adjustable gate valve (VAT) to ensure work in at a desirable pressure. Typical gas flow rates were in the 30-50 sccm range, and the operational pressure was selected between 0.7 and 1.4 Pa because such pressure is low enough to allow sputtered atoms to travel to a substrate while high enough to allow stable operation of the magnetron discharge.

III. RESULTS

The experiments started with a silicon target which has slightly higher conductivity than boron but is similar to boron in many other characteristics. The purpose of using silicon was to establish a baseline of system's operation and performance. We could show that in spite of the relatively low conductivity of pure silicon, applying a pulsed voltage from the Pinnacle®Plus power supply allowed us to obtain a magnetron discharge with stable, reproducible ignition and operation in wide frequency range from few Hz to 350 kHz.

The situation was very different when switching to the boron target. In the desired operational pressure range of 0.7-1.4 Pa, applying a voltage from the Pinnacle®Plus did not ignite the magnetron discharge at any setting. We then tried to ignite an auxiliary glow discharge by applying a dc bias voltage to the substrate holder, which also did not ignite since the pressure is too low for a glow discharge. The ignition "trick" was to simultaneously apply both voltages: to the target from the Pinnacle®Plus, and to the substrate holder using the dc bias supply. The procedure of igniting was the following: The Pinnacle®Plus is set to its maximum frequency of 350 kHz and constant-power mode at 250 W. Without plasma, the power supply runs to its maximum open circuit voltage of 650 V (plus build-in "strike voltage" pulses of up to 1200 V). Then the dc power supply is switch on and its voltage gradually increased until the magnetron discharge ignited. The dc voltage necessary for ignition depends on the temperature of the boron target. At the beginning, when the boron target is still cold, the dc voltage needed was as high as 600-750 V. After ignition of the magnetron, the dc bias voltage can be reduced to a much lower level while keeping the magnetron discharge alive, which required a current from dc power supply in the range 10-40 mA. Once the surface of the boron target was at elevated temperature, in a matter of minutes, the dc bias power supply could be shutoff, or one could continue using it to affect the microstructure of the growing film. In any case, with the boron target at elevated temperature, the magnetron sputtering system can now operate in a self-sustaining regime, as shown in the photo of Fig.2.

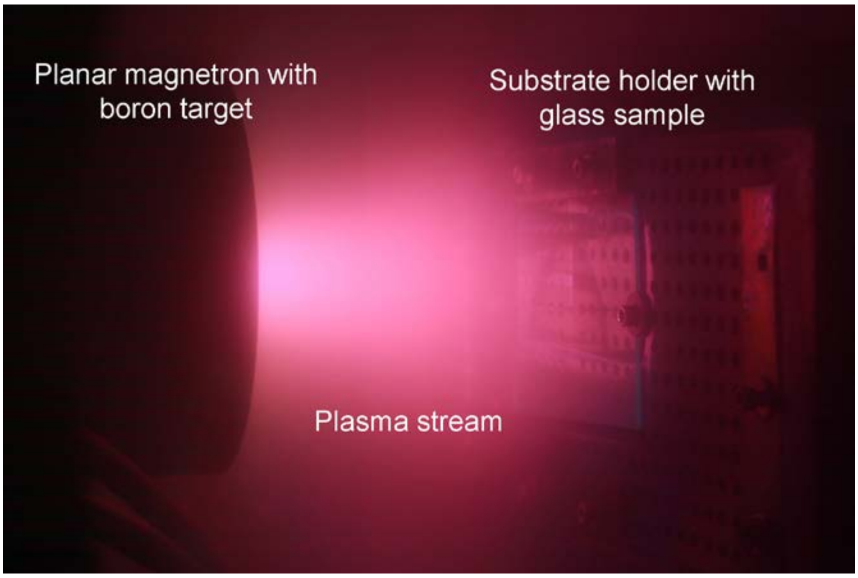

Fig. 2. Photo of the discharge system operating with a pure boron target shown the characteristic red color of the boron-containing plasma. The planar magnetron is to the left and substrate holder to the right, as indicated. Experimental conditions are: nitrogen pressure 1 Pa, frequency 350 kHz, discharge voltage 470 V, average discharge current 0.53 A, average discharge power (power-stabilized mode) 250 W.

As expected, the dc voltage required to ignite the magnetron with a boron target depends on pressure. In Fig. 3 one can see that increasing the pressure from 0.78 to 1.3 Pa leads to a decrease of the necessary dc ignition voltage from 750 V to 470 V.

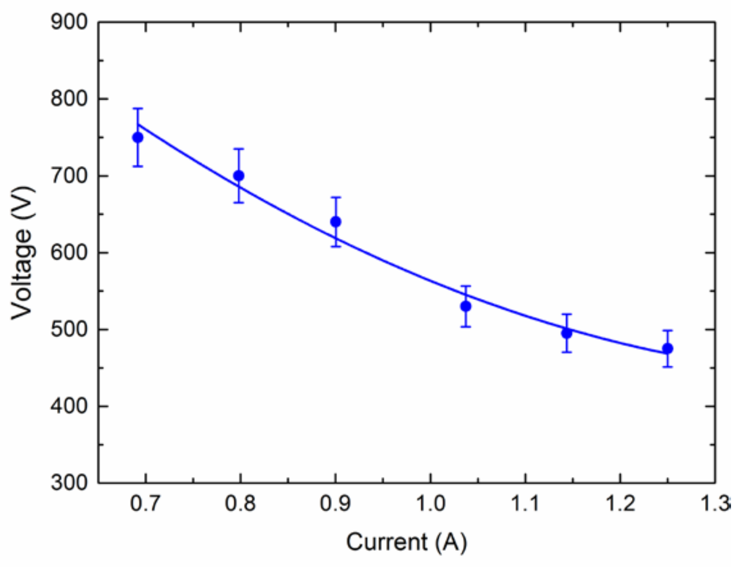

Fig. 3 Influence of nitrogen pressure on dc bias voltage necessary for the ignition of the magnetron discharge; boron target, setting to 150 W average power, 350 kHz.

Furthermore, the required dc ignition voltage can also be reduced by increasing the power set point of the Pinnacle®Plus, however, that effect is small since for ignition the open-circuit voltage is what matters most, and that voltage does not depend on the power setting.

The burning voltage slightly increases with increasing discharge current for a magnetron discharge with a boron target. As can be seen in Fig. 4, the discharge burning voltage increased by about 50 V from 410 V to 460 V when increasing the current from 0.4 to 0.7 A.

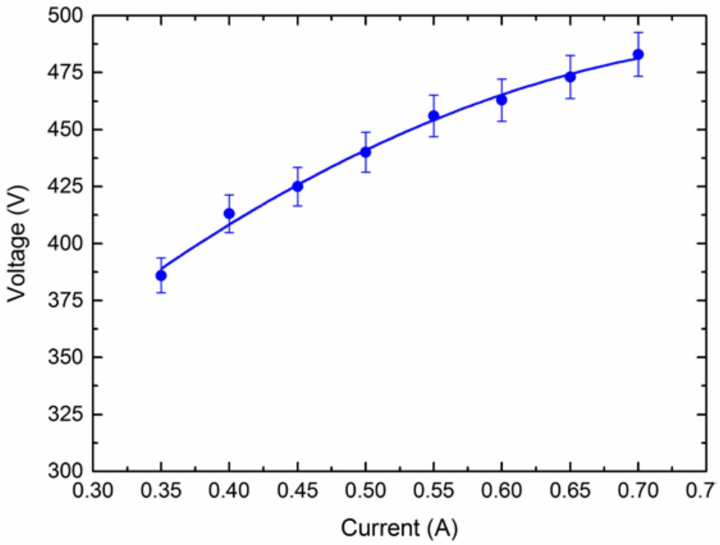

Fig.4. Current-voltage characteristic of a planar magnetron with a boron target; pressure 0.9 Pa (nitrogen), pulse frequency 350 kHz.

An influence of frequency on discharge operation, i.e. on discharge burning voltage and current in the power-stabilized mode, is clearly visible in Fig. 5. The lower the frequency of pulsing the higher the discharge voltage and thus, under constant power mode, the lower the discharge current. The discharge moves to more stable operation mode at high frequency as can be judged by the discharge self-adjusting to a lower voltage.

Several boron films were deposited for characterization and testing of film properties. The power-dependent deposition rate was determined by profilometry and taking into account the power settings.

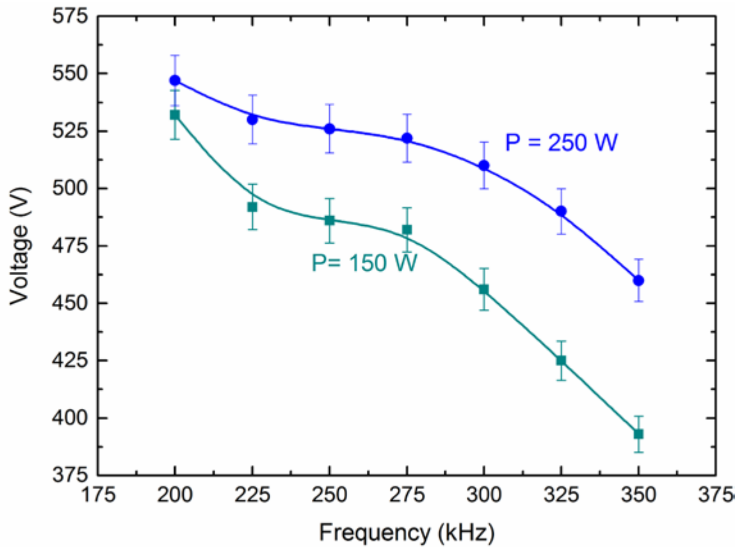

Fig.5. Influence of the nitrogen pressure on the bias voltage required for the ignition magnetron. Boron target; pressure 0.9 Pa (nitrogen); pulse frequency 350 kHz.

We found, at a pressure of 0.9 Pa nitrogen, and for the constant power mode at 250 W (current about 0.5 A and voltage about 500 V), a deposition rate was approximately 400 nm/hour. Similar values were determined at about the same pressure for argon, and at somewhat lower pressure (0.57 Pa) for oxygen. Film characterization was not part of this study and will be done separately.

IV. DISCUSSION

The key demonstration is that, despite having an essentially insulating target, it is possible to ignite a magnetron discharge without resorting to an RF power supply and its matching network. This was enabled by the simultaneous application of a dc bias to nearby part (the holder) and using a mid-frequency rectangular-pulse power supply. This allows a simplified approach to boron sputtering. The question is: what underlying features allowed this demonstration?

We point out that the mid-frequency power used here had rectangular pulse shape (as opposed to sine wave). Considering a Fourier analysis of such “rectangular” pulses, nominal of 350 kHz, such voltage type contains a large number of much higher frequencies. For an estimate one can consider the inverse rise and fall times of the pulses (~ 10 ns), and readily arrives at frequencies that contain and even exceed the standard RF frequency of 13.56 MHz.

The application of the additional dc bias of > 500 V allows for the production of additional electron-ion pairs that assist in the ignition of the main discharge, the magnetron discharge. Finally, boron is not a perfect dielectric but a semiconductor, showing increasing conductivity with increasing temperature. Therefore, even as the target is (indirectly) cooled by being mounted on a cooled magnetron assembly, it can reach elevated temperature (estimated a few 100°C) on its surface, where it is clamped. Current can therefore flow along the target surface to its periphery, where the conducing clamp ring can make the contact.

Using this picture, the observed relationships in terms of pressure, frequency, power set point etc. fit well in conventional understanding of the magnetron discharge.

V. SUMMARY AND CONCLUSIONS

A stable mode of pulsed planar magnetron operation with a pure boron target was demonstrated in the mid-frequency range up to 350 kHz, avoiding the cost and scaling-difficulties that come with using RF power supplies and their power-matching RF networks. The investigations focused on the discharge ignition process, identifying a method of ignition with a reasonable discharge parameters. The key to ignition was the addition of an assisting dc bias (> 500 V) temporarily applied to the substrate holder. The bias can be reduced (< 50 V) upon ignition and even completely removed once the surface of the boron target is at elevated temperature such as to conduct the discharge current to the target clamp. A relatively high deposition rate of about 400 nm/h has been found on samples placed 7 cm from the target for an average power of 250 W. The findings can be explained keeping in mind that the mid-frequency power pulses have high-frequency components that stretch in the RF-frequency range. Boron and boron nitride films have been deposited but the characterization of those films was not part of this report.

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