PLASMA-ENHANCED PULSED LASER DEPOSITION OF WIDE BANDGAP NITRIDES FOR SPACE POWER APPLICATIONS[1]

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ABSTRACT

The need for a reliable, inexpensive technology for small-scale space power applications where photovoltaic or chemical battery approaches are not feasible has prompted renewed interest in high-efficiency radioisotope-based energy conversion devices. Although a number of devices have been developed using a variety of semiconductors, the single most limiting factor remains the overall lifetime of the radioisotope battery. Recent advances in growth techniques for ultra-wide bandgap III-nitride semiconductors provide the means to explore a new group of materials with the promise of significant radiation resistance. Additional benefits resulting from the use of ultra-wide bandgap materials include a reduction in leakage current and higher operating voltage without a loss of energy transfer efficiency. This paper describes the development of a novel plasma-enhanced pulsed laser deposition system for the growth of cubic boron nitride semiconducting thin films, which will be used to construct pn junction devices for alphavoltaic applications.

INTRODUCTION

Alphavoltaic Device Concept

There are a number of space power applications where sufficient quantities of solar photons are not available, and chemical-based battery technology is not an optimum choice. As a result, there has been renewed interest recently in the concept of a radioisotope based battery, which is a potential alternative to solar and chemical based technologies. The concept has been described by a number of authors [1-5], and reviewed in detail by Olsen [6]. The basic idea consists of capturing highly energetic particles (such as those emitted from various radioisotopes) by a semiconductor device capable of converting the particle energy to electrical energy. Perhaps the most significant demonstration of the concept to date used silicon pn junction diodes with Pm-147 as a source of beta particles to obtain peak powers of 400 μW in a physical package suitable for pacemaker applications [6]. The functionality of such a device is presently limited by tradeoffs resulting from the damage threshold of the semiconductor material versus the amount of available energy per particle, as well as the stopping power of the material for a specific particle type and energy. Concentrating on absorbing MeV-range alpha particles can theoretically lead to a higher energy conversion efficiency due to the comparatively large stopping power of most semiconductors for such particles, but this simultaneously leads to a probable reduction in overall device lifetime [7]. Therefore, in order to provide both the necessary output power levels and overall system lifetime, a suitable semiconductor with the required degree of radiation tolerance must be identified.

For the radioisotopes of interest, the energy of a single alpha particle is on the order of several MeV (5.5 MeV if using Am-241). Therefore, the bandgap energy of the semiconductor is largely irrelevant from a particle absorption standpoint. In fact, a single particle has sufficient energy to generate hundreds of thousands of electron-hole pairs or more. From a device perspective, then, a larger bandgap energy is preferred, as it will lead

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to a reduction in reverse leakage current and a higher value for the maximum attainable open circuit voltage. A larger bandgap energy also implies the potential for better radiation resistance due to generally stronger bond strengths. Rybicki, et. al. have demonstrated a SiC-based alphavoltaic battery, and although they found a significant initial power output, a degradation of 58% after 100 hours of exposure to a 5 millicurie Am-241 sample was observed [7]. In order to realize an alphavoltaic device with a useful lifetime, then, it is necessary to look to materials with even greater radiation resistance.

Cubic Boron Nitride

There exist a number of ultra-wide bandgap materials which, until recently, have been regarded more as insulators than actual semiconductors. Among these, diamond and the cubic phase of boron nitride exhibit a number of interesting properties beyond bandgap energies on the order of 6 eV, including hardness and good thermal conductivity (table 1). Although diamond appears to be an attractive candidate, especially as it has been found to be reasonably radiation-tolerant, so far efforts to obtain n-type diamond in particular have not yet produced the desired material [8,9]. In contrast, amphoteric doping has been possible in bulk samples of cubic boron nitride (formed by high temperature, high pressure techniques) for some time using beryllium and silicon [10]. In fact, reference [10] describes the fabrication of a blue/ultraviolet emitting pn junction fabricated from cubic boron nitride, strongly suggesting the potential for successfully fabricating a pn junction diode from the material for use in a high-energy betavoltaic or alphavoltaic application.

Table 1. Selected properties of h-BN, c-BN and diamond.

Property	hexagonal BN	cubic BN	Diamond
Density (g/cm^3)	2.26	3.45	3.52
Melting Point (K)	-	> 3000	3800
Lattice Constant (Å)	c=2.5, a = 6.661	3.615	3.567
Hardness (kg/mm^2)	-	9000	10000
Stiffness (10^{11} $dyne/cm^2$)	33	71	-
Energy (eV)	3.63	6.4	5.45
Rel. Dielectric Constant	3.8	7.1	5.5
Doping Capabilities	-	n-type, p-type	p-type

OVERVIEW OF CUBIC BORON NITRIDE FILM GROWTH

Although fabrication of bulk cubic boron nitride is relatively straightforward (it is available commercially in powder form for example, at approximately $25/gram), single phase thin films of cubic boron nitride still remain elusive despite numerous attempts using a variety of growth techniques [11-28]. Both chemical and physical vapor deposition techniques have been employed, both with and without some type of ion source. Many authors have reported the existence of the cubic phase of boron nitride in films grown by these and related methods, but there is no strong evidence that any cubic material has been obtained without the use of simultaneous ion bombardment, either pure N_2 or nitrogen-containing mixtures. Of all the methods discussed in the literature, the most popular seems to be ion-assisted pulsed laser deposition [17-23], which has produced some of the most convincingly cubic-containing films to date. However, there are no reports of actual nucleation of 100% cubic boron nitride, largely due to the extraordinary lattice mismatch between the film and the (001) silicon substrates commonly employed. Instead, the interfacial layer is almost always reported to be amorphous or at best a mixture of amorphous and turbostratic phases of boron nitride. However, there are reliable reports of films containing at least some fraction of the cubic phase, indicating that the cubic phase is formed some time after film nucleation.

Reference 24 describes a mechanism whereby the crucial parameter determining whether a film is cubic or not is actually the momentum of the bombarding ions. The fact that a number of groups have reported a relatively sharp threshold in terms of the bombarding ion energy (and hence the ion momentum) required to obtain

cubic as opposed to purely hexagonal films lends support to this explanation. Furthermore, almost all ion-assisted reports (mostly Kauffman-type ion sources) mention that resputtering of the film is observed if the ion energy is further increased, so that a window of ion energy exists in which it is possible to obtain cubic-containing films. There still exists some question as to the exact mechanisms at work, but compressive stress induced by ion bombardment is consistent with the fabrication techniques employed to form bulk samples of cubic boron nitride. However, although it is clear that ion bombardment plays a role in the formation of the cubic phase, it is also clear that some type of activated nitrogen is required in order to grow stoichiometric films, as the binding energy of molecular nitrogen is 9.9 eV. Substrate temperatures sufficient to disassociate the nitrogen are impractical, so an alternative is required.

Another difficulty encountered in duplicating reported techniques for successful growth of mostly cubic boron nitride thin films is that there exist a number of complications in almost every type of characterization measurement employed. The result is a great deal of skepticism with regard to whether thin films (< 1000 Å) on substrates with enormous lattice mismatch to cubic boron nitride (e.g. silicon, the most commonly employed substrate) possess more than a small fraction of cubic sp^3 bonded material. Although infrared measurements frequently suggest the presence of sp^3 bonded BN, there also exists a wurtzitic phase of BN that is also sp^3 bonded. Perhaps the most detailed description of such difficulties is given in reference 27, which suggests that many reports of cubic boron nitride films are in error, in part because of similarities between the signature features of the hexagonal and cubic phases, as well as interactions involving the silicon substrate that can lead to the incorrect conclusion that the cubic BN phase is present. The authors of reference 27 even point out that some of their own work incorrectly led to the conclusion that cubic boron nitride had been deposited, due to contamination of the sample with copper, which is closely lattice matched to cubic boron nitride. Thus, it will likely be necessary to achieve a distinctly high quality single phase film of cubic boron nitride that can be characterized by luminescence-based techniques in order to unambiguously establish a technique as successful.

In order to achieve device-quality p- and n-type single-phase thin layers of cubic boron nitride, it is unlikely that the phase conversion/compressive strain/ion bombardment approach will prove sufficient. Even if nearly 100% of the film could be converted to the cubic phase, the extremely high defect density resulting from both ion bombardment and severe lattice mismatch between the film and typical substrate choices will make the realization of efficient devices impossible. Beyond such critical issues, it should also be pointed out that the film growth techniques described result in amorphous or polycrystalline morphologies characterized by grain sizes typically on the order of 100 Å, which can also seriously reduce device efficiency through grain boundary transport effects. In order to realize practical devices, a different approach is clearly required. In this work, a pulsed laser deposition system has been modified to incorporate an inductively coupled nitrogen plasma source capable of delivering atomic nitrogen to the surface of the growing film, in contrast to ionized molecular nitrogen. The necessary boron flux is provided through ablation of a pure boron target by a pulsed ultraviolet-wavelength laser.

PLASMA-ENHANCED PULSED LASER DEPOSITION

Technique Description

Pulsed laser deposition (PLD) is a common technique for growth of a variety of thin film materials, including insulating coatings, superconducting ceramics and semiconductors. Depending on deposition parameters (especially substrate temperature), amorphous, polycrystalline or single-crystal epitaxial layers may be formed. The basic technique consists of mounting a target inside a vacuum chamber in proximity to a heated substrate. The target is evaporated by focusing a laser beam through a window, usually with the target rotated to prevent cratering and to maximize the target life (Figure 1). Initially PLD was accomplished using Q-switched Nd:YAG lasers, which typically provide ~10-100 mJ in a pulse of approximately 10 ns duration, delivering on the order of megawatts of optical power to the ablation target. However, infrared lasers such as the Nd:YAG (λ = 1064 nm) ablate the target through a thermal process, which is typically characterized by a nontrivial amount of particulate expulsion that can seriously affect the film morphology. It is now common practice to employ an ultraviolet wavelength laser such as an ArF or XeCl excimer (λ = 193 nm and 308 nm, respectively) or even a frequency tripled or quadrupled Nd:YAG laser (λ = 355 nm and 266 nm, respectively). The ultraviolet wavelengths appear to ablate many targets through a more electronic (i.e. bond-breaking) process rather than a purely thermal process, resulting in significantly reduced particulate damage to the growing film. Although it is essentially a

physical vapor deposition technique, PLD presents a number of interesting opportunities for enhanced chemical interaction at the substrate, as the vapor plume leaving the ablation target is frequently associated with a plasma, especially if there is any interaction between the plume and the incoming laser beam. The introduction of reactive gases or dense plasmas other than those generated by the laser ablation process can be also be used in PLD, providing the opportunity for unique types of non-equilibrium film growth processes.

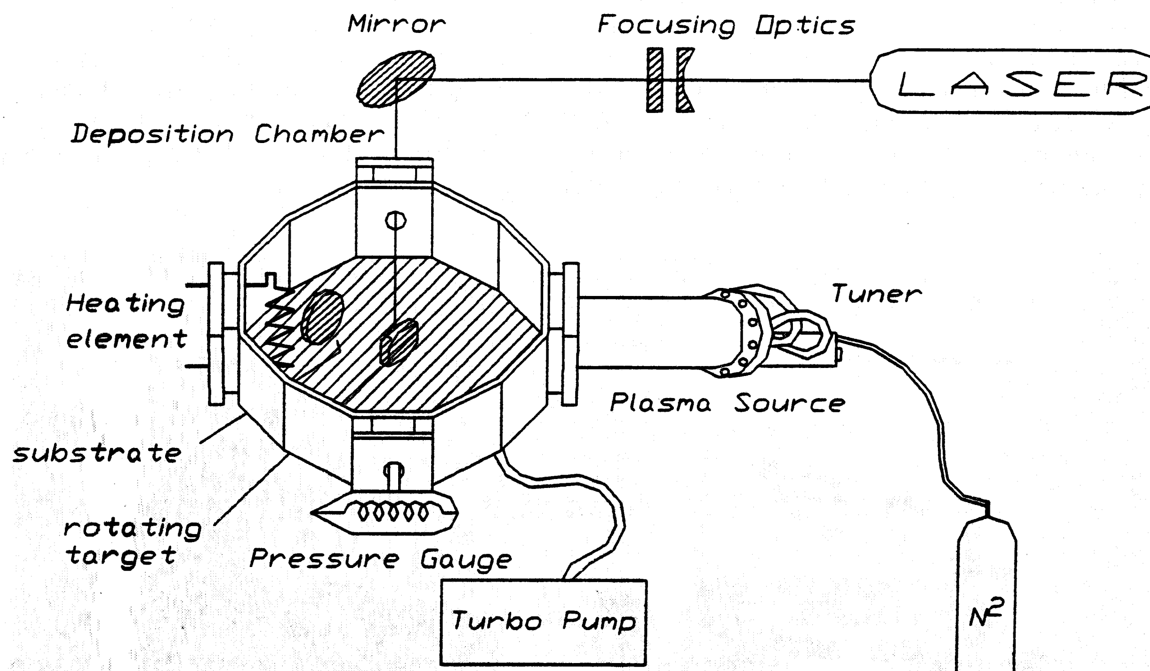

Figure 1: Schematic of plasma-enhanced pulsed laser deposition system.

Chamber Description/ Experimental Setup

Although a number of groups have attempted laser-based techniques for growth of cubic boron nitride, only ion-assisted methods seem to be successful, at least from a reproducibility standpoint. In all cases, however, the actual process seems to be a conversion of the growing film from non-cubic phases to some type of partially-cubic mixed-phase material, most likely in response to ion bombardment. Recent comparison studies of molecular beam epitaxy (MBE) growth of GaN material using different types of nitrogen sources suggest that an alternative may be possible. Hughes, et. al. recently compared an electron cyclotron resonance (ECR) plasma source and an inductively coupled RF plasma source under similar conditions to determine which source is better suited to growth of high-quality GaN [28]. As part of the study, the emission spectra from both plasma sources were measured using a monochrometer [28]. Results of the measurements indicate that the ECR source produces a plasma that contains a large fraction of excited states of both neutral and ionized molecular nitrogen, but very little atomic nitrogen (at least under the power levels and N_2 flow rates employed) [28]. In direct contrast to this, excited states of atomic nitrogen were observed using the RF source, and no evidence of molecular nitrogen ions was found [28]. The conclusion of the study (based on characterization of the GaN films) was that the RF source was superior to the ECR source, most likely due to the ability of the source to deliver atomic nitrogen to the growing film.

Based on the MBE-based GaN literature, an existing PLD vacuum chamber was modified to include an EPI model EPI-RF-450-G-N UNI-Bulb N_2 RF plasma source (Figure 2). Since the EPI source was designed for use in an MBE system, it was necessary to modify the configuration in order to install the unit on the PLD chamber. In particular, an external sleeve was required over the plasma source to accommodate the 12.5" in-vacuum length of the unit and to match the 4.5" conflat plasma source flange to the 2.75" conflat flange on the PLD chamber. Also, a tantalum extension tube (Figure 3) was mounted on the plasma source to direct the plasma

into the PLD chamber and towards the substrate assembly. A capacitive tuning unit is then mounted directly on the end of the plasma source, and is used to provide impedance matching between the 600 W 13.56 MHz RF power supply and the plasma source. Operation of the plasma source consists of first pumping down the chamber to ~1×10^{-8} Torr base pressure using a turbomolecular pump, and then introducing 99.9995% purity N_2 gas through a leak valve mounted on the plasma source. The RF power supply is dialed to a setpoint of 200 W, and the tuning unit is used to adjust for any impedance mismatch. If the plasma does not ignite at that point, the flow rate of N_2 must be temporarily increased. Once a plasma has been established, there exists an appreciable impedance mismatch, as the plasma now acts as a lossy secondary inductance coupled to the plasma source coils. Typical chamber pressures during the presence of a high-brightness plasma are on the order of 5×10^{-5} to 1×10^{-4} Torr. The most dramatic visual effect is the intense orange glow emanating from the plasma source, in contrast to the purplish glow observed in capacitively-coupled RF and ECR nitrogen plasmas. According to the spectroscopic analysis in reference 28, the orange plasma corresponds to excited states of atomic nitrogen, and the purple glow in other N_2 plasmas corresponds to the 1st negative transitions of N_2^+ molecular ions.

Figure 2: Photograph of PLD system modified to include nitrogen plasma source. The tuning unit used to minimize reflected power is shown unmounted and off to the left in the photo.

The source of boron for growth of BN films is a 99.9% purity 1" diameter x 0.25" thick boron target mounted on a rotating holder. This is one of the advantages to using PLD as opposed to thermal evaporation techniques such as MBE: low vapor pressure targets such as boron can be evaporated easily without the need for high-temperature sources. The rotation of the target prevents cratering where the laser is focused, and increases the lifetime of the target. The laser presently used is a frequency quadrupled (λ = 266 nm) Spectra Physics model DCR3G Nd:YAG laser, which is also capable of operation at 1064, 532 and 355 nm. The ultraviolet lines (266 and 355 nm) are preferable for laser ablation, in that the target is ablated more smoothly and less particulate emission is obtained than with infrared lines. Up to 80 mJ per pulse (~ 5 ns for the 266 nm line) can be focused through the laser port window onto the target to obtain a boron flux. The heated substrate is parallel to the target, with the distance adjustable from about 1.5 to 4". At present, there is no means of measuring the boron or atomic nitrogen

fluxes in-situ, so they must be estimated by measuring the film thickness after growth. With the plasma source on-line, present efforts are directed towards initial depositions of BN films, and characterization by Xray diffraction, FTIR, SEM and optical spectroscopy. Once adequate material quality is obtained, the next phase is to explore both in-situ and ex-situ means of doping the layers in order to form pn junction diodes for testing under alpha and beta particle irradiation.

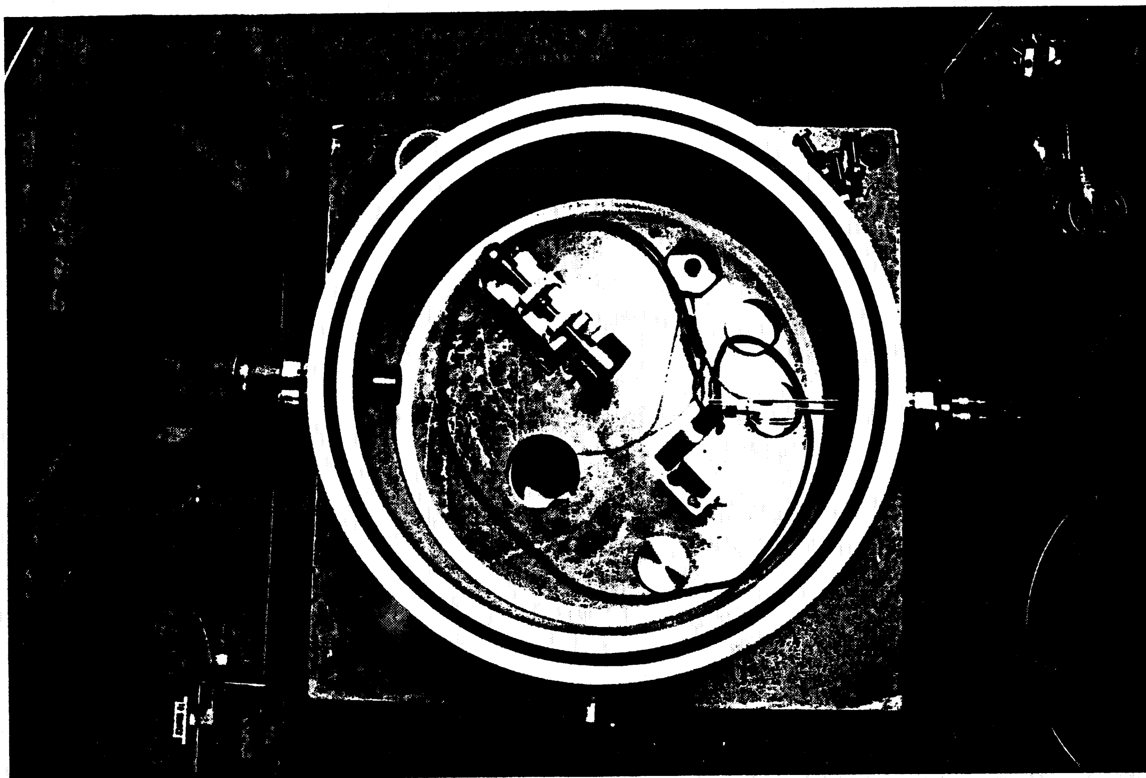

Figure 3: Interior view showing tantalum extension tube used to direct plasma flow. The substrate mounting assembly and target rotator are not in growth position, where the extension tube lines up with the substrate.

SUMMARY

In order to effectively implement the concept of an alphavoltaic device, it is necessary to develop the capability to fabricate devices with a significant degree of radiation resistance. The best possible approach is to utilize a material with an inherent ability to withstand the expected radiation environment, such as cubic boron nitride. Additional benefits of cubic boron nitride based devices include a reduction in leakage current and large open circuit voltages as a result of the ultra-wide bandgap (~6.4 eV). Previous attempts to obtain high-quality single phase thin films of the material have resulted in mixed phase or amorphous films, with any cubic content resulting from compressive strain induced by ion bombardment. An alternative approach to cubic boron nitride film growth is proposed, in which atomic nitrogen is provided directly to the substrate in what is termed plasma-enhanced pulsed laser deposition. The non-equilibrium growth inherent to PLD in conjunction with atomic nitrogen is expected to provide the means to directly nucleate the cubic phase in order to obtain device-quality semiconductor material.

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