

# Design and synthesis of novel thin films and structures by reactive crossed-beam laser ablation

Philip R. Willmott,<sup>\*a,b</sup> Hannes Spillmann<sup>a</sup> and J. Robert Huber<sup>a</sup>

<sup>a</sup>Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

<sup>b</sup>Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen, Switzerland.  
 E-mail: philip.willmott@psi.ch

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As new materials are discovered, there is a strong drive to include them in thin film form as micro- and nanostructures. Established growth techniques may be unable to meet the demands required of these often chemically and crystallographically complex materials. An account is given of pulsed laser deposition (PLD) and its novel extension, pulsed reactive crossed-beam laser ablation (PRCLA) as possible alternative methods for the non-thermal synthesis and growth of novel advanced materials. After a brief description of the principles and applications of PLD, it is shown that adding a synchronized pulsed gas source can lend both technical and fundamental advantages. Examples of syntheses of thin films and multilayer structures of novel and technologically relevant materials are then described.

## Emerging materials and thin film techniques

An important challenge in modern condensed matter physics is the discovery and characterization of novel materials and their exploitation in areas as diverse as biophysics, optoelectronics, and nanotechnology.<sup>1</sup> As our understanding of the properties of materials deepens, there is an increasing change in the approach to this problem. The philosophy can be increasingly encompassed by the concept of “materials by design”: no longer are substances fabricated, and their possible applications subsequently investigated. Instead, the main goal is now to recognize a problem that needs to be resolved by materials design and then to achieve this by using the wealth of knowledge gained over the last two to three decades in the fields of solid state chemistry and physics. This has been made possible by an increased competence in theoretical modelling of materials<sup>2</sup> and by the development of novel synthetic techniques for producing new chemical systems. This need for materials by design is becoming more urgent as typical device sizes continue to fall below micron dimensions, and heterogeneous materials are integrated in a single device. It is therefore essential to understand the fundamental processes and microscopic mechanisms at work in order to control film deposition.

Many of the emerging “smart” materials tend to have complicated stoichiometries and crystal structures.<sup>3,4</sup> Established growth processes, such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE), that have sufficed for the deposition of simple elemental, binary, or binary solid solution materials are unlikely candidates for the fabrication of chemically complex thin films. In addition, the incorporation of novel materials in, for example, standard silicon technology presents problems of crystallographic incommensurability and

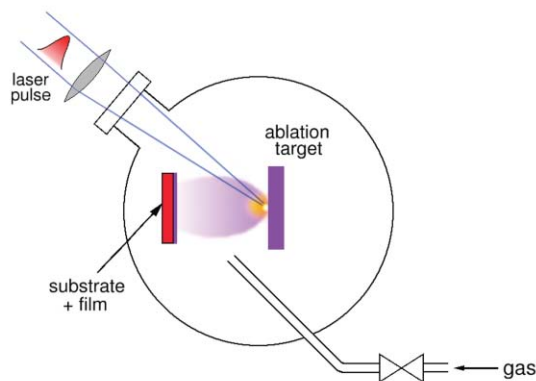
incompatible thermodynamic properties. The ability to deposit films under *non-thermal conditions* may alleviate such difficulties.

The regime of non-thermal interactions in its most general sense describes physical and chemical processes such as the breaking and making of chemical bonds by ensembles of species that have energy distributions that do not follow a statistical, Maxwell–Boltzmann distribution and therefore cannot be described by a single temperature.<sup>5,6</sup> Such distributions can be achieved if energy from an external source (for example, from a laser or an electric discharge) can be selectively pumped into a particular degree of freedom which is effectively or temporarily decoupled from the rest of the molecular or atomic system. In practice, this becomes attractive if activation barriers can be transcended or indeed lowered by non-thermally exciting selected degrees of freedom.

Soon after their introduction in the Sixties, it was recognized that high-powered pulsed lasers could be used as flexible and powerful tools for studying the interaction of intense electromagnetic fields with solid material.<sup>7</sup> A general feature of the so-called ablation plasmas that are thereby produced is their extremely high ion and electron temperatures, of the order of several thousand Kelvin, and their high degree of ionization. The dominant mechanisms were found to depend sensitively on laser parameters such as the energy fluence (laser energy per unit area), pulse duration  $\tau$ , laser wavelength, polarization, and laser repetition rate, as well as on the chemical and physical properties of the material being irradiated. Theoretical models describing light–material interactions and the subsequent liberation of gas-phase species have become increasingly sophisticated as more experimental data have become available.<sup>5,8,9</sup>

## High power lasers used for film growth

The problem of making high quality thin layers of complicated materials has been tackled by developing new deposition methods capable of handling these substances. A particularly successful and flexible technique is pulsed laser deposition (PLD).<sup>10</sup> The principle of PLD is simple and is shown in Fig. 1. Material is very rapidly evaporated from a bulk “target” in a vacuum chamber by focussing a high power laser pulse on its surface, each pulse being about 10 ns in duration and having an energy of typically 0.1 J (equating to a power flux of the order of 1 GW cm<sup>-2</sup> for a 1 mm<sup>2</sup> focal spot). The focused light produces such a large electric field that some of the electrons within the optical absorption depth of the material are rapidly stripped from their atoms. They oscillate in the electromagnetic field of the laser light, and also collide with neighbouring atoms



**Fig. 1** The principle of pulsed laser deposition. A laser pulse is focused onto a target material inside a vacuum chamber. The resulting ablation plasma, or “plume”, expands and can recondense on a substrate placed in its path. The chemistry of the film can be modified by the addition of a reactive background gas.

or ions, thereby transferring some of their energy to the lattice within this surface region of the target. These processes have characteristic times on a picosecond scale and occur while the laser pulse impinges on the target surface. After the laser pulse is extinguished (approximately 10 ns), a very hot cloud of vaporized material, typically of 10 000 K or more, has been generated, which is commonly referred to as a laser plasma. This process is called laser ablation. Material is transferred by the rapid expansion of the cloud of vaporized, or “ablated” material, caused by Coulomb repulsion and recoil from the target surface. Recondensation of the gas phase material can then occur on a substrate placed in the path of the expanding plasma. Following each laser pulse, the amount of material deposited on the substrate is tiny, of the order of 1/100th of a monolayer, but after repeating this process several tens of thousands of times, a film with a thickness of the order of 1  $\mu\text{m}$  will have formed on the substrate. Indeed, the unique pulsed nature of deposition in PLD makes it an ideal tool for studying growth processes *in situ* and in real time using techniques such as RHEED<sup>11</sup> or surface X-ray diffraction.<sup>12</sup>

Nanosecond ablation dominates PLD research. It is, however, rather inefficient. A typical 100 mJ, 10 ns pulse may liberate  $10^{15}$  atoms.<sup>13</sup> Even assuming an extreme case in which each atom has a kinetic energy of 100 eV, is singly ionized (the first ionization potentials for many elements lie around 10 eV), and also emits a 5 eV photon, less than 20 % of the laser pulse energy is accounted for. Most of the energy is coupled to the bulk in the form of heat by efficient transfer *via* the nascent plasma during the laser pulse. Indeed, at a laser repetition rate of 10 Hz, the time-averaged incoming power is typically 1 W. This corresponds very accurately to the emitted black-body radiation of the ablation target (corrected by the spectral emissivity curve), which is heated by approximately 50 K.

Ablation using femtosecond lasers has attracted much attention recently as a powerful technique for optimal material removal.<sup>14</sup> The advantage lies primarily in the ability to couple all the photonic energy to the electrons in the ablated material before they can, in turn, couple to the lattice (which takes some picoseconds). The ablation efficiency is thereby increased by a factor of 10 to 100 or, alternatively, the ablation threshold is correspondingly lowered. One consequence of this is that there is very little or no collateral damage to the material immediately adjacent to the ablation region, which in ns ablation can result in the ejection of macroscopic particles, or “laser droplets” (see below). Femtosecond ablation is rarely exploited as a deposition technique, however, primarily due to the high cost and inconvenience of operating femtosecond lasers and amplifiers.

Perhaps the most remarkable aspect of PLD is that the

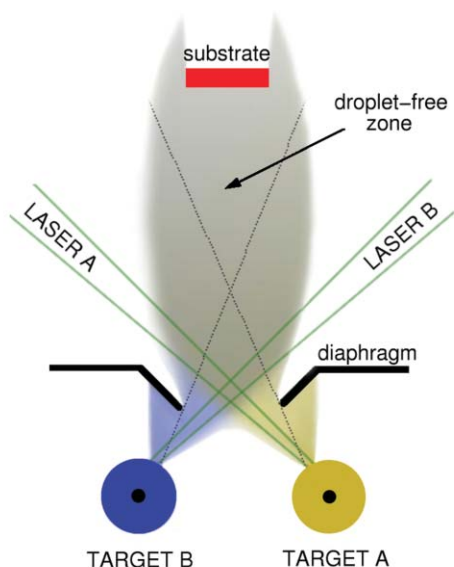
deposited layer not only has, in general, the same stoichiometry as that of the target material, but also the same crystal structure. For example, it was possible to grow Nd- and Cr-doped  $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$  garnet with 160 atoms per unit cell heteroepitaxially on Si(001) using PLD. Because of this property, PLD has become increasingly popular within research laboratories as a flexible method of producing thin films of novel materials, especially since its successful application in the growth of commercial  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  cuprate superconductor thin film devices in the late Eighties.<sup>15</sup> Despite this, PLD has still to fulfil its commercial promise, particularly in semiconductor applications, in which the necessity of device grade purity and high crystallographic perfection has proved to be the major stumbling block.

A further problem is the production of so-called “laser droplets”.<sup>10</sup> These are macroscopic (typically micron-sized) particles ejected from the surface of the ablation target that become incorporated in the growing film, thereby undermining its homogeneity and quality. The production of laser droplets represents a great obstacle to the use of PLD in commercial applications. Their occurrence results from *subsurface boiling*, *recoil ejection*, and *exfoliation*. The first two of these are termed “splashing” phenomena and, to a first approximation, are independent of the target morphology and can produce droplets from a single laser shot. Subsurface boiling will occur in materials in which the time needed to convert laser energy into heat and transfer it into the bulk is shorter than the time needed to evaporate the surface layer, defined as having a thickness of the order of the skin depth of the material  $\delta$ . This explosive phase transition is negligible in dielectric materials due to their generally low thermal conductivity. In metals with low melting temperatures and high thermal conductivities (*e.g.* Al) however, this process may be dominant and can only be suppressed by using sufficiently low laser fluences or short (femtosecond) laser pulses, with the attendant reduction in the ablation yield. This sets important limitations on the choice of laser radiation used in PLD.

When the transient melt below the laser focus spot is subjected to the recoil pressure exerted by the expanding ablation plasma, droplets can be ejected as the melt is squeezed onto the solid bulk. As the typical sizes of droplets from recoil ejection and subsurface boiling are similar, it is hard to distinguish between them, though the angular distribution in recoil ejection has more of a crown form than that in subsurface boiling, which shows a  $\cos^n\theta$  dependence.

The final hydrodynamic effect is termed “exfoliation” and describes particulate ejection due to increased surface roughening by repeated melt–freeze cycles of the irradiated material. Eventually, the macroscopic outgrowths become necked off and thermally decoupled, and break away as particulates. These may have dimensions of many microns, depending on the material. Because exfoliation is a morphological process that requires two or more laser shots, it can often be avoided by careful target surface preparation and refreshment. This can be achieved either by continuously repositioning the target so a fresh surface is exposed at each laser pulse<sup>10</sup> or by using liquid targets (see below).<sup>16,17</sup>

A recent adaptation of PLD has resolved the droplet problem, though at the cost of an additional laser source. Tselev *et al.* have ablated two targets, separated by approximately 1 cm, simultaneously.<sup>18</sup> The two plumes in Fig. 2 collide with each other, as the number density is still high. They are scattered forwards towards the substrate, and the points of ablation can be masked from the direct line of sight of the substrate, thereby excluding the incorporation of droplets, which are too heavy to be scattered by the ablation plume. This has two additional advantages: (a) more chemically complicated and novel material can be created using two different target types, and (b) the angular distribution of the scattered



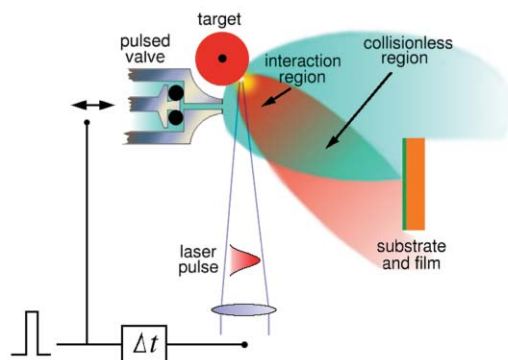
**Fig. 2** The incorporation of droplets in films grown by PLD can be avoided by using two ablation sources and letting the plumes interact close to their origins where the number density is high enough to allow multiple collisions. The resulting mixed plume is scattered forward to the substrate, while any droplets produced by the ablation process are too heavy to be significantly scattered. The substrate is therefore screened from the droplets in a droplet-free zone in the shadow region of an appropriately positioned diaphragm. Adapted from Tselev *et al.*<sup>18</sup>

crossed plume is greater than in conventional PLD, reducing the problem of spatial inhomogeneity in the film growth rate.

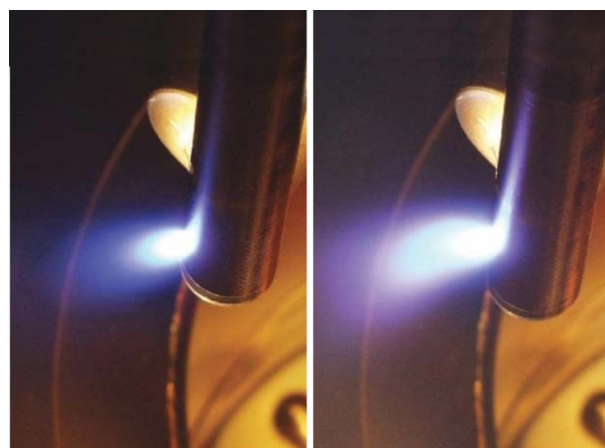
Organic thin films are also provoking great interest as templates for potentially cheap and flexible optoelectronic devices.<sup>19</sup> The use of *ultraviolet* nanosecond radiation for PLD of organic materials has shown only limited success, due to extensive photochemical decomposition of the organic structure in the ablation process. Not surprisingly, the functionality of the organic material is to a large extent lost when the atoms and ions recondense on the substrate surface. Recent work using femtosecond tuneable *infrared* light from a free electron laser has shown enormous promise in overcoming this problem.<sup>20</sup> By tuning the light to a specific vibrational mode of the organic material, large, functionally intact, fragments can be non-thermally removed from the ablation target, and the resulting films show essentially identical properties to the bulk material. The goal now is to find an alternative cheap and appropriate tuneable infrared pulsed light source.

### Gas pulses increase the degrees of freedom

A modification of PLD has been pioneered at the University of Zürich.<sup>6,21</sup> The PLD setup shown in Fig. 1 has been adapted by the addition of a pulsed gas valve placed next to the ablation target, as shown in Fig. 3. In this manner, it is possible to release gas in temporally ( $\sim 300 \mu\text{s}$ ) and spatially localized packets synchronized with the laser light pulses. The timing of the gas pulse and the laser pulse is controlled so that the ablation plasma is produced just as the densest portion of the gas pulse emerging from the valve nozzle passes in front of the point on the target where the laser is focused. As the plasma expands and propagates through the gas pulse, it transfers some of its energy from the plasma species to the gas particles *via* collisions in this transiently relatively high pressure region, with number densities of the order of  $10^{15} \text{ cm}^{-3}$ . This enhances the chemical reactivity of the gas pulse particles, which can then partake in reactions with the plasma particles.<sup>22</sup> This has a dramatic effect on the appearance of the ablation plume, which becomes significantly brighter and larger (see Fig. 4).



**Fig. 3** Principle of pulsed reactive crossed-beam laser ablation. A pulsed valve is placed close to the laser focus on the ablation target rod. The laser is triggered after a controlled delay of  $\Delta t$  after the pulsed valve trigger, chosen so that the ablation plume interacts with through the densest part of the gas pulse, thereby exciting the gas pulse species. Both the gas pulse species and the plasma species then continue to expand adiabatically and rapidly become collisionless, thereby maintaining their reactivity.



**Fig. 4** The visual effect of crossing the ablation plasma with a gas pulse. The left picture shows the ablation of Zr metal in vacuum. In the right picture, taken with identical exposure settings, the ablation plasma is crossed with an  $\text{N}_2$  gas pulse and becomes brighter and larger.

The interaction of the ablation plume with the gas pulse means that gases can be used which would under normal conditions not be sufficiently chemically reactive. An example is the production of GaN, an important optical semiconductor material, from the ablation of Ga with  $\text{N}_2$ , which can otherwise only be produced at much higher temperatures and nitrogen gas pressures.<sup>17</sup> A fundamental advantage of using a gas pulse is that after its interaction with the ablation plasma, it rapidly expands into a vacuum, the distance between the gas particles increases, and collisions become rare. Therefore, species excited by the collisions that occur before the pulse has expanded enough maintain their reactivity as they rapidly enter collisionless conditions. In contrast, if one employs a constant background of gas, the initial collisions and excitation occur, but then the reactivity is lost again as the particles continue to collide with the background species all the way to the substrate and ultimately become rethermalized.

It is noteworthy that although reactive species are formed by plasma–gas pulse interactions, associative chemistry first takes place primarily on the surface of the substrate. In the gas phase interaction region where the plasma crosses the gas pulse, there is too much energy for chemical bonds to form permanently; only when the species reach the surface can the substrate remove the excess energy and allow bonds to be formed and a

film to grow. This is in contrast to the famous Smalley source for cluster formation, in which the collisions between the gas pulse and ablation plasma occur within a constricted volume,<sup>23</sup> with the result that collisions with the walls cause rapid cooling and the formation of the desired clusters. For epitaxial film growth, clusters should be avoided, and our system therefore allows free expansion of the ablation and gas beams. The use of a synchronized pulsed gas source also lends the technique technological advantages: because the gas is only present during the ablation process, the gas load on the pumping system is greatly reduced, while impurities in a continuous background gas that could become incorporated between ablation events are also avoided.

This powerful adaptation of PLD has been termed pulsed reactive crossed-beam laser ablation, or PRCLA. It is most suited for the growth of thin films of materials for which one subset of elements comes from the ablation target, and the second subset from the gas pulse. Hence, simple materials such as CuO can be produced by the ablation of Cu in conjunction with an oxygen gas pulse,<sup>21</sup> while more complicated materials can also be created, such as ZrAlCN (ZACN) from the ablation of a Zr–Al target in a nitrogen–methane mixture gas pulse.<sup>24</sup>

### Optical semiconductor thin films grown with PRCLA

We concentrate on three examples of films synthesized using PLD and PRCLA to demonstrate their power and flexibility. The search for a reliable direct bandgap semiconductor that emits in the blue and ultraviolet region of the spectrum has been the holy grail of the semiconductor industry since the Seventies. The potential market in data storage devices, flat panel full color luminescent displays and telecommunications is worth billions of dollars. Research into blue light-emitting devices was, however, plagued with problems until the early Nineties. The most intensely investigated materials had been the II–VI compound semi-conductors, such as ZnSe, ZnS, CdSe, and CdS. The primary reason why these materials were chosen was because of their high crystallographic compatibility with established Si and GaAs technology. They failed because of their low bond strengths: “seed” crystallographic faults would propagate catastrophically under the influence of high energy photons within the material, and device lifetimes, even at cryogenic temperatures, were measured in minutes.

In 1989, Shuji Nakamura began research into the III–V nitride semiconductors, particularly GaN, InN, AlN and their solid solutions<sup>25</sup> as possible alternative candidates for large bandgap optical semiconductors. The bandgap energy of the family AlGaInN spans 1.95 to 6.2 eV, with only an 11% lattice mismatch between the two extremes, AlN and InN. Before, these compounds had been rejected on account of the lack of a suitable substrate material: even the most commonly used substrate for GaN growth, sapphire, has a 14% mismatch, and the “best” substrate material, SiC, has a mismatch of 3%. However, the bond strength of the nitrides is far greater than those of the sulfides and selenides, and crystallographic faults therefore remain isolated. By 1998, the group led by Nakamura had demonstrated room temperature laser action for over 10 000 h using a Ga<sub>1-x</sub>In<sub>x</sub>N/GaN quantum well device. The ascendancy of these materials now seems assured. There remain, however, important challenges to improve device properties. Primary among these is a lowering of the processing temperature, which should lead to a reduction of the inter-diffusion layer and improved integration of AlGaInN with Si and GaAs technology. Growth of AlGaInN using PLD, with its non-thermal nature, is therefore a tantalizing avenue of research.

Attempts have been made to achieve this goal, with varied success. All methods that employ volatile Ga precursors also contain hydrogen, which has been shown to neutralize

p-doping when incorporated in the film unless it is annealed above 700 °C. A successful alternative technique has been PLD, in which three different approaches have been attempted. In the simplest approach, a sintered GaN target is ablated.<sup>26</sup> However, the material purity is rarely better than one part in 10 000, which, being significantly larger than the intentional dopant concentration, falls far short of the purity required for semiconductor applications.

The purity of electronics grade Ga metal, ammonia, and N<sub>2</sub> is, however, sufficient for high quality film growth. Attempts to grow GaN by reactive PLD using a liquid Ga ablation target were successful using static NH<sub>3</sub> as the ambient,<sup>27</sup> but only became possible with N<sub>2</sub> at pressures of the order of 10<sup>2</sup> Pa.<sup>28</sup> In the third approach, GaN and Al<sub>x</sub>Ga<sub>1-x</sub>N were grown in our laboratories using PRCLA at low average background gas pressures.<sup>17,29</sup> It was shown that by using this method, two long-standing problems could be resolved. Firstly, it was possible to grow GaN and Al<sub>x</sub>Ga<sub>1-x</sub>N at low temperatures without hydrogen-containing precursors, and secondly, by using high purity material, the problems associated with sintered ablation targets could be circumvented. The effect of the nitriding source on the growth kinetics and the subsequent film quality was also shown to be critical.

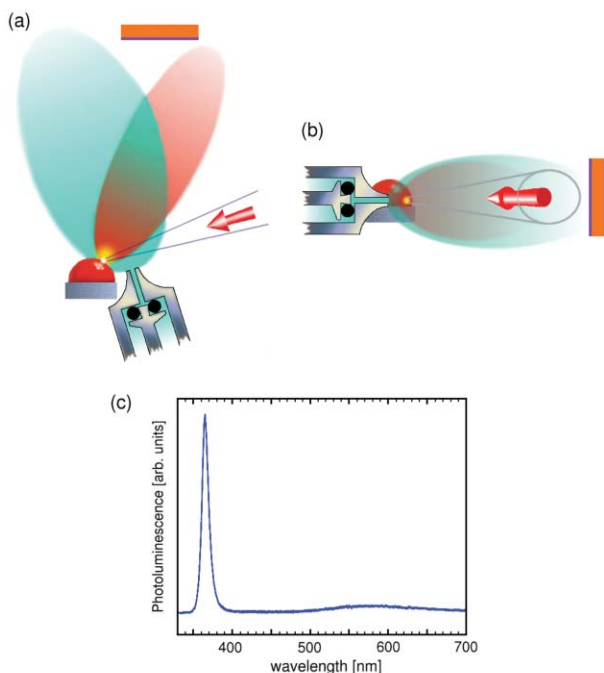
Ga has a melting temperature of 28 °C, and so rapidly melts under laser radiation. On the other hand, it is well known that solid Al produces large amounts of laser droplets by exfoliation under ns ablation. The ablation target was therefore a liquid Ga–Al alloy in a crucible heater that could heat efficiently up to 750 °C. Using a liquid target meant that the production of laser droplets by exfoliation was completely avoided.<sup>16,27</sup> Further important advantages of using liquid ablation targets over sintered targets include higher purity, ease of preparing targets with different Ga–Al ratios, and low cost. Two experimental geometries are shown in Fig. 5. In the “vertical” geometry, the laser light impinges at a near vertical angle onto the liquid target [Fig. 5(a)]. Although this is in principle the simpler design, many research laboratories do not have the facility to introduce laser light into a vacuum chamber from above. The second design avoids this problem by heating a volume of metal that is sufficiently larger than the crucible cup that the meniscus approximates an oblate ellipsoid form which is vertical some 2 mm above the edge of the crucible. This region can then be ablated by the more conventional arrangement of a *horizontally* impinging focused laser beam [Fig. 5(b)].

Heteroepitaxial growth of GaN(0001) and Al<sub>x</sub>Ga<sub>1-x</sub>N(0001) films on Si(111) was demonstrated using PRCLA of Ga and an N<sub>2</sub> pulse. Collisions in the interaction region activated the N<sub>2</sub> sufficiently that full nitridation was guaranteed. Fig. 5(c) shows an example of the photoluminescence spectrum of GaN grown by PRCLA on Si(111).

### Transition metal carbonitrides—hardness made to measure

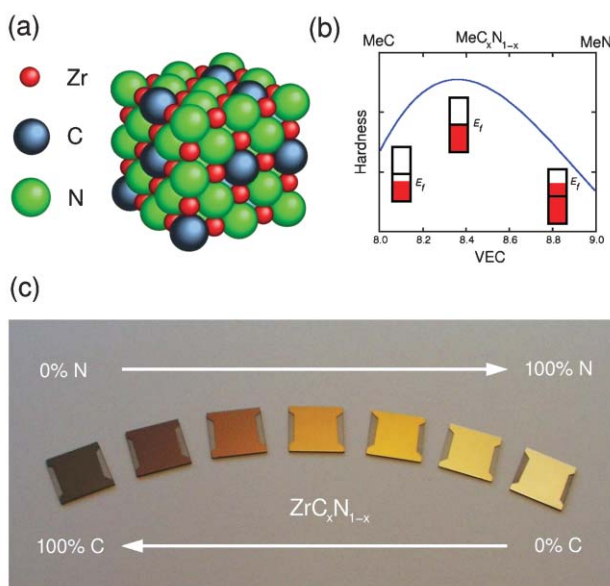
The second example concerns tribological coatings. In the search for hard coating materials, much more than hardness alone is desired. The material should also have good wear properties, have a low coefficient of friction, and be chemically stable. It has long been known that the transition metal nitrides and carbides are promising hard materials. Titanium nitride, a prototypical compound, has been used as a coating on drill and latheing tools for several years, in order to improve their cutting strength and useful lifetimes.

Slightly more complicated systems are the transition metal carbonitrides, which can be thought of as an alloy of the pure nitride and pure carbide. Their general chemical formula is MC<sub>x</sub>N<sub>1-x</sub>, where M designates the transition metal and *x* runs from 0 to 1, illustrated in Fig. 6(a). An interesting empirically discovered property of the carbonitrides is that although the



**Fig. 5** Schematic diagram of the experimental setups used for the production of GaN and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  thin films. (a) A vertical setup can be used, where the laser impinges on the liquid target from above. (b) If the liquid has a sufficiently high surface tension, a horizontal setup can also be employed (shown here in side view), where the liquid forms a meniscus which is vertical at one point. (c) Room temperature photoluminescence spectrum of a GaN film grown using PRCLA. The sharp peak at 364 nm corresponds to the energy gap of the optical semiconductor.

pure carbide is marginally harder than the pure nitride, the hardest composition lies between the two binary limits.<sup>30</sup> This material is an ideally suited candidate for growth using PRCLA, and demonstrates the technique's flexibility. It was discovered that by changing the relative mixture of methane



**Fig. 6** (a) Transition metal carbonitrides are solid solutions with a rocksalt structure. The carbon and nitrogen anions are shown as large blue or green spheres, while the metals (small red spheres) sit in the cationic sites. (b) The hardness of transition metal carbonitrides shows a maximum for a valence electron concentration of 8.4. (c) The colour of the carbonitride changes from grey/black for the pure carbide to silvery yellow for the pure nitride.

and nitrogen in the gas pulse, the chemical composition of the material (*i.e.* the value of  $x$ ) can be easily controlled.

We have grown exceedingly pure  $\text{ZrC}_x\text{N}_{1-x}$  thin films in the range  $x = 0$  to 1 by PRCLA in our laboratory, using a zirconium rod that is ablated in the presence of a nitrogen–methane mixture gas pulse.<sup>24</sup> By using high purity materials, we can avoid the incorporation of unwanted impurities, particularly oxygen, which undermine the film quality. Although marginally less hard than their titanium-based equivalent compounds, we chose zirconium as the transition metal, as its carbonitrides have much lower frictional properties than those of other transition metal carbonitrides. A further modification was made, in which we replaced the zirconium ablation target with a Zr–Al alloy to produce  $\text{Zr}_{0.8}\text{Al}_{0.2}\text{C}_x\text{N}_{1-x}$  (ZACN). Partial substitution of Zr with Al allows the formation of a thin aluminium oxide layer on the surface, which protects the film from further oxidation at elevated temperatures, also an important property for cutting tools or systems working in aggressive atmospheres.

A recent theoretical model of these systems by Cohen and coworkers proposes that their hardness depends fundamentally on their electronic properties, see Fig. 6(b).<sup>30</sup> Because nitrogen has one more electron than carbon, the electronic properties of  $\text{ZrC}_x\text{N}_{1-x}$  change smoothly between the two binary limits. The relevant parameter here is the valence electron concentration (VEC), defined as the number of valence electrons in a formula unit. ZrC therefore has a VEC of  $4 + 4 = 8$ , while that of ZrN is  $4 + 5 = 9$ . The model predicts that at about  $\text{VEC} = 8.4$ , an electronic band is completely filled. This is shown to be resistant to shear strain, *i.e.* its energy increases upon distortion. The shear modulus of a material is directly related to its hardness. The next band lying immediately above this, in contrast, drops in energy due to mechanical distortion of the crystal and so any electrons occupying this band will contribute to a weakening of the material. The optimum stoichiometry is therefore one in which the lower band is completely filled, and the upper band unoccupied. The model predicts that this occurs for a composition of  $\text{ZrC}_{0.6}\text{N}_{0.4}$ , while for ZACN it is  $\text{Zr}_{0.8}\text{Al}_{0.2}\text{C}_{0.4}\text{N}_{0.6}$ , which we experimentally verified for sets of films of  $\text{ZrC}_x\text{N}_{1-x}$  and ZACN over the whole range  $0 \leq x \leq 1$ .<sup>24,31</sup>

The colour of the carbonitrides is also affected by their composition. The more nitrogen there is in them (*i.e.* as  $x$  gets smaller), the larger is the material's electron density (nitrogen is pentavalent while carbon is tetravalent). The more free electrons there are in a material, the more reflective it is. This has a remarkable effect on the appearance of the carbonitrides, as shown in Fig. 6(c). Pure zirconium carbide is dark grey. As the composition changes gradually to the pure carbide, and carbon atoms are gradually replaced with nitrogen atoms, the electron density increases, and the material becomes increasingly reflective, until for pure zirconium nitride, it is a silvery yellow.

### Tailored structures—the best of all worlds?

Periodic multilayer structures consisting of successive bilayers  $(\text{AB})_n$  are known to display superior hardnesses than either component A or B. This is because all real materials have hardnesses that fall far short of that predicted by theory for a perfect crystal, due to the fact that crystalline imperfections such as vacancies, dislocations, and chemical impurities are points of weakness that can promote the propagation of microcracks, leading eventually to material failure. These cracks can be effectively terminated at crystal boundaries, hence material in a compact polycrystalline form tends to be robuster than in the form of a single crystal. In the same manner, a regular array of such boundaries can be created by depositing alternate ultrathin layers on top of one another. The layer boundaries pin the microcracks, halting their progress. To work effectively,

however, the interfaces have to be abrupt and the materials A and B should be chosen so that they have quite distinct shear moduli.

PLD lends itself admirably to the growth of multilayer structures by the use of compound or multiple targets.<sup>32</sup> We have gone one step further and grown novel periodic four-sublayer structures of  $(\text{ZrC}_x\text{N}_{1-x}/\text{VC}_x\text{N}_{1-x}/\text{TiC}_x\text{N}_{1-x}/\text{VC}_x\text{N}_{1-x})_n$ .<sup>33</sup> The reasoning behind growing these structures runs as follows. The carbonitrides are in general harder than the pure nitrides or carbides, as already mentioned.  $\text{ZrC}_x\text{N}_{1-x}$  has a very low coefficient of friction, though is less hard than the Ti-based carbonitride. Their shear moduli are, however, uncomfortably close to one another, hence a third material was chosen with a weaker shear modulus to separate them.  $\text{VC}_x\text{N}_{1-x}$  was chosen because the transition metal V is pentavalent and ablates cleanly using nanosecond laser pulses. Thus, the carbon to nitrogen ratio leading to the optimal VEC of 8.4 for the tetravalent transition metal carbonitrides (*i.e.*  $x = 0.6$ ), produces a VEC of 9.4 in  $\text{VC}_x\text{N}_{1-x}$ , which should therefore be significantly weaker.

Such thin films were grown by PRCLA using a composite Zr–V–Ti target rod and  $\text{CH}_4$ – $\text{N}_2$  gas mixtures for the gas pulse. Initial experiments showed a nanohardness of some 40 GPa, an enhancement of 20% compared to the corresponding multilayers lacking the  $\text{VC}_x\text{N}_{1-x}$  buffer layers.<sup>33</sup> It is thought that further tuning of the growth parameters should improve the hardness still further.

## Conclusions and outlook

PRCLA has been shown to be an excellent method for the synthesis of many novel and technologically important materials in the form of thin films. It has been used to produce, among others, optical and lasing materials, semiconductors, superconductors, and superhard materials. The potential areas of applications are very broad, from biocompatible coatings for prosthetic hip replacements to electronic devices. In the near future, the main interest will lie in combining and integrating several different materials as thin films on one device in multilayer structures in ways that have, until now, proven to be impossible. By combining materials in this unusual way, it is hoped this will lead to further new phenomena in materials science.

Until now, the commercial use of PLD and PRCLA has been limited to the production of magnetic sensors using high temperature superconducting materials. The extension of these methods to other commercial areas has been held back by the established nature of more conventional techniques. Another reason is the relatively small area that can be deposited evenly using the very directed laser plasma from a single ablation target and the relatively high cost of high power laser sources. It has been shown, however, that there is no technically insurmountable problem in upscaling these novel techniques for deposition of larger areas. When the power, flexibility and elegance of PLD and PRCLA become more widely recognized, and as the need to use new and ever more complicated materials in thin film production increases, their unique qualities should mean that their commercial application will become attractive.

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