Front. Energy 2022, 16(4): 542–547
https://doi.org/10.1007/s11708-022-0834-8

VIEWPOINT

Qian LI, Jing LIU

Liquid metal printing opening the way for energy conservation in semiconductor manufacturing industry

For nearly a century, semiconductor has kept playing an extremely important role in promoting the advancement of modern science, technology and society, owing to its performance advantages and industry-driven feature. Surprisingly, when the time comes to this day and age, the semiconductor area, which is entering into its 3rd generation era, even develops much rapidly than ever before. Overall, the semiconductor industry is mainly driven by three generations of materials. The first generation, represented by silicon (Si) and germanium (Ge), began from the 1950s. The second generation, represented by gallium arsenide (GaAs) and indium phosphide (InP), emerged from the 1980s. The third generation, focusing on those of gallium nitride (GaN) and silicon carbide (SiC), dated back to the late 20th century. The semiconductor industry, as the most capital, human and technology-intensive manufacturing area, is often faced with such a tough challenge: before the production begins, water and electricity have to be in place. Up to the present, nearly all the classical semiconductor growth technologies such as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), metal-organic chemical vapor deposition (MOCVD), and atomic layer deposition (ALD) etc. have been relying heavily on high temperature processing and perfect vacuum conditions (Figs. 1(a) and 1(b)), which were basically subjected to large power stability. Taking the chip as an example, its manufacturing is among the most complicated ones spanning various disciplines, interlocking from the initial wafer production and cutting on the production line to the final packaging, checking and testing, etc. The whole process usually covers dozens of complicated procedures. Any errors occurred over the process would lead to ultimate wafer scrap and subsequent huge loss. Therefore, for a semiconductor manufacturing enterprise, its power supply often has to withstand very high power quality, and huge energy consumption costs. To a large extent, the semiconductor industry can be regarded as a big electricity consuming society, whose energy conservation and consumption reduction is therefore a must but not just a necessity.

Recently, from an alternative other than the conventional high temperature manufacturing, Li et al. [1] proposed the room temperature printing of large area and wide bandgap ultrathin quasi-2D GaN semiconductor. As the first ever trial in the field, this method is made possible through introducing plasma mediated confined nitridation reaction of the printed liquid metal gallium (Fig. 1(c)). The new conceptual chemical reaction formula was thus established as $N_2 + 2Ga \xrightarrow{\text{Plasma at} \sim 25°\text{C}} 2GaN$. As almost an iron law in nature, nitrogen is always treated as a classical inert gas that could not react directly with gallium even at a high temperature. But now this elementary knowledge might be updated since the plasma reaction has made the dream of room temperature nitridation of gallium a reality. The core mechanism lying behind the phenomena is that, the administrated nitrogen plasma is in a thermodynamically excited stable state and ionic form, and the activation energy of such chemical reaction is thus pretty low and makes it possible to easily generate GaN semiconductor based on the direct reaction between nitrogen plasma and liquid Ga. Previously, classical ways to prepare GaN films are usually working at high temperatures such as MOCVD (approximately 950 °C–1050 °C) and ALD (> 250 °C) (Figs. 1(a) and 1(b)). Meanwhile, toxic material often could not easily be avoided. These are definitely not favorable for a large scale industrial production of semiconductors. For example, one typical method to manufacture GaN depends on the MOCVD reaction, i.e., $Ga(CH_3)_3 + NH_3 \xrightarrow{\text{Above } 950°\text{C}}$

Received Jun. 17, 2022; accepted Jul. 11, 2022; online Aug. 20, 2022

Qian LI
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Jing LIU (✉)
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China; Department of Biomedical Engineering, School of Medicine, Tsinghua University, Beijing 100084, China
E-mail: jliu@mail.ipc.ac.cn

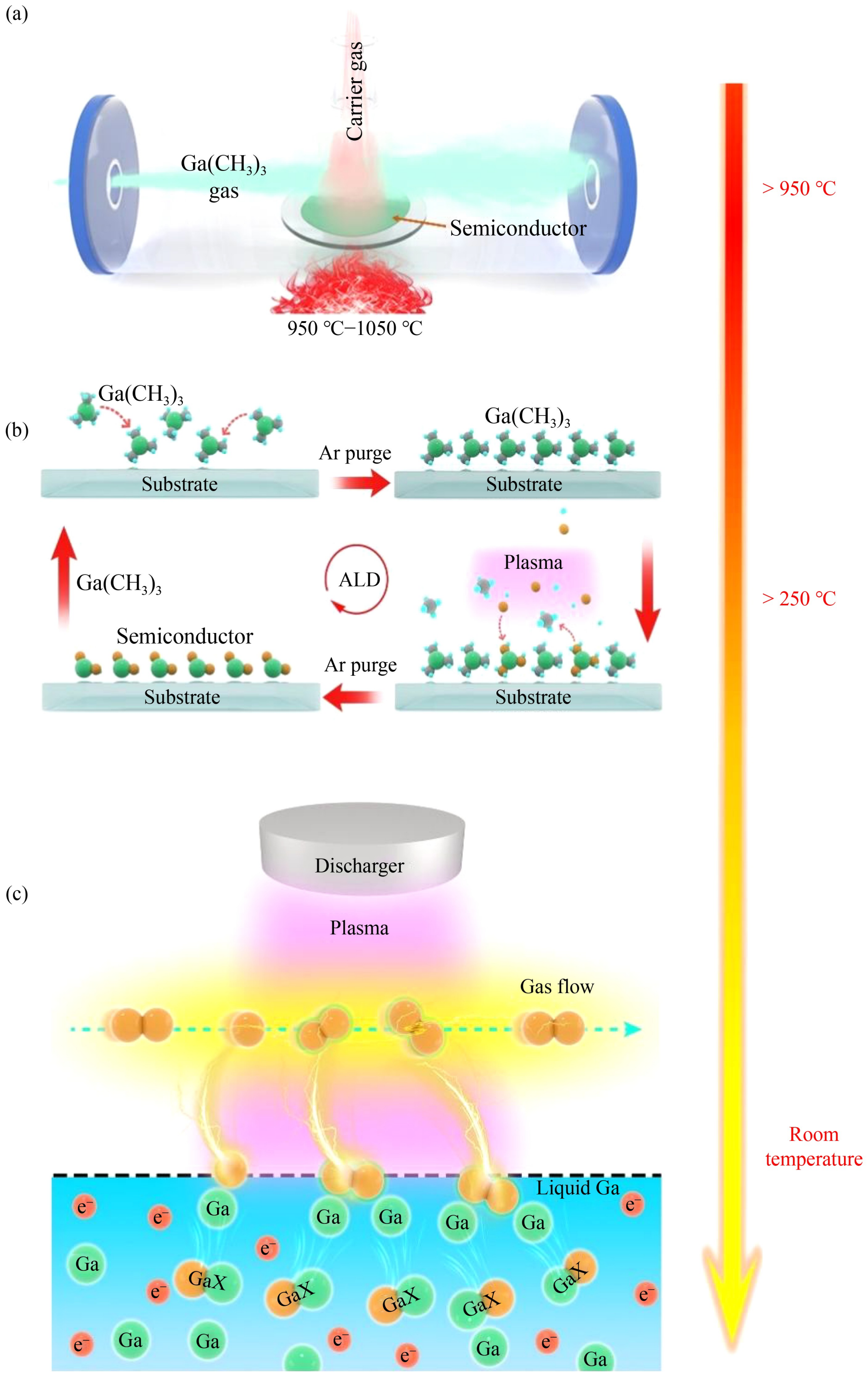

Fig. 1 Three representative principles to manufacture semiconductor and their working temperature conditions (Redrawn from Ref. [1]). (a) MOCVD way to manufacture semiconductor at a temperature of 950 °C–1050 °C; (b) ALD method to make semiconductor, requesting temperature above 250 °C; (c) gas or plasma mediated chemical reaction of liquid metal gallium for room temperature manufacture of semiconductors, at approximately 25 °C.

$GaN + 3CH_4$. On the contrary, the latest finding [1] opens an easy going way for significantly reducing the energy and related cost in the manufacture of pivotal semiconductor GaN. Most noteworthy still lies in that, such room temperature printing has generalized purpose and allows to produce the GaN with a thickness spanning from 1 nm to above 20 nm, also known as quasi-2D semiconductors and remarkable candidates for making high quality microelectronic devices. This implies a certain new start of the semiconductor industry. Although at this stage, the method is still not finalized enough, plenty of solutions are available to further furnish the procedures. For example, regarding the potential defects present in the printed GaN films, rapid thermal annealing can be adopted to effectively eliminate crystal defects. As is widely known, the semiconductor technology has been accompanied by the study of lattice defects since its inception, while in practice, defective crystals do not necessarily lead to inferior devices, and semiconductors that are chemically and structurally intact can be adopted in tuning the material properties. Meanwhile, both controlling (reducing, eliminating) defects and exploiting them would improve performance and yield of the device. In addition, more alternatives can be tried in the coming future.

In fact, manufacture of electronics and semiconductor via energy conservation and environment friendly way has long been an ambitious goal for the whole electronic industry. In 2012, Zhang et al. [2] systematically proposed a brand new strategy over conventional ways to achieve true direct writing or printing of electronics including semiconductor materials through introducing the electronic inks made of low-melting point liquid metals or their alloys. The core principle is to first print liquid metal to form specific electronic patterns and then chemically process them to realize *in situ* the target semiconductor. They specifically illustrated several typical ways to make semiconductors via liquid metal printing and allied processing such as oxidation, nitridation and more chemical modification including ion implantation under the assistance of external energy like laser, microwave, or plasma, etc. As outlined therein, many different types of semiconductors such as liquid metal oxides (e.g., gallium oxide or indium oxide), GaN, Ga_2S_3, $AgGaS_2$, GaSe, GaAs etc. can thus be manufactured via such a straightforward way. In this sense, even an integrated circuit incorporating all necessary electrical elements and matching semiconductors can be printed in a moment. Such a game changing technology is abbreviated as DREAM Ink (direct writing of electronics based on alloy and metal ink), implying the dream of electronics fabrication. Since 2014, a series of commercial liquid metal printers as well as electronic product thus made have been gradually translated into industry [3]. Recently, with more research laboratories over the world joining together, the time has come for the liquid metal printed electronics area to be fully explored. It should be pointed out that, potential semiconductors that can be printed via liquid metal are rather diverse. Of the many possible candidates, gallium oxide is the easiest to be used in ambient air at room temperature. By disclosing the wetting mechanisms of the naturally formed gallium oxide in modifying the liquid metal electronic inks, Gao et al. [4] demonstrated the first ever liquid metal printing or writing of functional electronics on either soft or rigid substrates such as epoxy resin board, glass, plastic, silica gel, paper, cotton, textiles, cloth and fiber etc. As now a gradually well understood liquid metal printed semiconductor, the oxide layer can easily form on the surface of liquid metals such as gallium under atmospheric conditions and at room temperature [2,4]. Even further, this nanometer scale oxide layer is in fact an ideal two-dimensional ultra-thin semiconductor planar material, which can adhere well to nearly all commonly used electronic device substrates (such as SiO_2 or Si), while the parent metal cannot [5]. This allows to firmly print liquid metal circuits or semiconductors on the target surface to realize various electronic functions. In fact, the liquid metal printing has generalized purposes. Except for quickly making the metal oxide, more other chemicals or their combinations can also be adopted to make a variety of semiconductors with the desired functions [2].

Up to the present, a series of representative semiconductors such as Ga_2O_3 [6,7], Bi_2O_3 [8], In_2O_3, SnO [9], and SnO_2 [10] have been obtained in laboratories worldwide via the printing of liquid metals, although some of the methods still rely on high temperature environment up to several hundred centigrade high and require the chemical processing of several steps. Overall, with an excellent solubility, fluidity, and reactivity, liquid metals can serve well as solvents, reactants and interfaces, and their combination with certain post-treatment processes would further make it possible for the preparation of more semiconductor materials, such as $GaPO_4$ [11], GaN [1,12], GaS [13], Ga_2S_3 [14], whether they are layered or non-layered in nature. Further, it should be mentioned that the currently available liquid metal printed semiconductors are still limited. But as time goes on, a great many opportunities can still be possible through continuous exploration. For example, as has been proposed before, by following the basic principle of liquid metal material genome [15], tremendous liquid metal materials can be screened out which can then serve as the initial seeds for the printed semiconductors. In addition, more liquid metal structured material such as MXene framework nanosheet [16] or liquid metal based semiconducting composites [17] can also be adopted for making potential semiconductor. In a word, the successful practice of room temperature printing of semiconductors like GaN [1], Ga_2O_3 [6,9] etc. suggests that new manufacture routes for reshaping modern electronic industries are already on the way.

As the first generation semiconductor material, Si is the most widely used, which forms the basis of nearly all logic devices, various types of discrete devices, and in the extremely common application of integrated circuits, information network engineering, functional products, aerospace engineering, and photovoltaic industry etc. The second generation semiconductor materials are mainly used to develop high-frequency as well as light-emitting electronic devices, and are excellent materials for making high-performance microwave and millimeter-wave devices and light-emitting devices. They are also widely used in satellite communications, mobile communications, optical communications and the Global Positioning System (GPS) navigation and other areas. The third generation of semiconductors owns a wider forbidden band width than the previous two generations, and is therefore also called wide forbidden band semiconductor. In particular, such materials represented by GaN, zinc oxide (ZnO), SiC, diamond, and aluminum nitride (AlN) display superior performances compared to silicon-based semiconductors, like high frequency, high efficiency, high power, high voltage resistance, high temperature resistance, and high radiation resistance etc. To a large extent, as former trials disclosed, liquid metal room temperature printing is closely correlated with nearly all the above semiconductor industries. This further indicates its unique value in significantly reducing the energy consumptions and environmental protections therein. In modern society, industry has clearly realized that broadband semiconductors can achieve functions that are difficult to do with silicon materials. Such semiconductors could also lead to higher performances and lower systemic costs in some areas that intersect with silicon materials, and therefore are regarded as key players in the post-Moore era. Further, nowadays the rising demand for electricity and low-carbon environmental protection makes it an immediate need to fully use smarter and more efficient ways of energy production, transmission, distribution, and storage. To get rid of the dependence on traditional fossil fuels and reduce environmental pollution, governments over the world have started to vigorously develop renewable energy industries, and the research exploration and development of liquid metal printed semiconductors might provide an ever important support for the transformation of new energy sources. Since the wide-band semiconductor can provide low impedance to reduce conduction loss and achieve energy efficiency, it is therefore regarded as a disruptive technology in the field of power electronics. Liquid metal printing will further enhance this endeavor as well as usher in a new era of manufacture. Without any doubt, the technology revolution inspired from liquid metal electronic inks, printing methodologies and practical applications is always on the way. The semiconductor and its cost effective printing is bound to become the firm cornerstone as essential elements and material processing core pillars of the coming industry.

Distinguished from traditional methods such as chemical vapor depositions that require high temperature, high vacuum, high energy consumption and complex processes, semiconductor materials created at room temperature from liquid metal have now started their journey. Such liquid metal semiconductor printing is straightforward and stable, cost effective, efficient, and energy saving. It does not depend on the nature of the substrate material. According to needs, the liquid metal inks can be deposited on various desired surfaces including those low-cost flexible materials such as plastic, paper, and fabric. This would significantly enhance the pervasive making and use of soft electronics. Particularly, it can achieve large area printing with batch manufacturing capability. The benefit is rather clear. Integrated circuit chip processing can currently be achieved with a maximum wafer diameter of 300 mm, while printed semiconductors and devices can be in an area of more than 1 m in diameter. Because of the reactive, non-polarizing and templating nature of liquid metals, they can provide many effective solutions to meet the current technical challenges of semiconductors requiring lower costs and energy consumption. In the traditional semiconductor preparation process, the temperature in the furnace can be up to 1000°C. For example, the power consumption of an industrial silicon furnace is 6300 kVA. Except for the fact that the acid washing does not consume too much electricity, the others are high energy consumption. But once the acid discharged from the silicon cores and rods is not treated properly when pickling, it easily leads to pollution to the environment. Liquid metal printing of semiconductor, on the contrary, is low-cost and environmentally friendly. Such low-cost comes from the metal raw materials and printing equipment. A device would possibly handle all the printing manufacturing process. Although a complete comparison between the gains in power consumption of different methods depends on their specific working situations and is beyond the scope of this paper, the output from the new method is rather promising and huge, say turning from MOCVD (950°C–1050°C) and ALD (above 250°C) to the current room temperature manufacture at approximately 25°C (Fig. 1). Moreover, the printing style based on additive manufacturing is entirely green. On the one hand, such manufacturing saves raw materials and reduces the potential pollution. On the other hand, the printing modality itself does not rely on the high temperature process, which therefore saves a lot of energy and reduces carbon emissions. Overall, the liquid metal printed preparations of a wide range of semiconductor materials and high-performance functional devices have been successfully initiated. As more technological advances and fundamental discoveries continue to be made in this area, such semiconductor printing would have an ever important impact on the coming energy society and environmental protection.

It should be pointed out that, while liquid metal printed semiconductor materials offer many opportunities for the next-generation high-performance electronics as well as integrated circuits, this area is still in its incubation stage and faces many technical challenges. First, at the material level, the variety of semiconductor materials obtained via single-element liquid metal oxides is still limited. The selection of suitable metals for alloying with liquid metals can expand the system of semiconductor materials. Currently, the most commonly used liquid metals are gallium and its alloys. However, from the thermodynamic point of view, the Gibbs free energy of Ga_2O_3 generation is –998.3 kJ/mol. For metals with a higher Gibbs free energy of oxide generation than gallium (Ga_2O_3), it is impossible to co-alloy with gallium-based liquid metals. Therefore, the range of liquid metals used to make semiconductor materials should be expanded to provide more options, such as indium (In_2O_3, –830.7 kJ/mol), tin (SnO_2, –515.8 kJ/mol), and bismuth (Bi_2O_3, –493.7 kJ/mol) or a combination of alloy oxide etc. From the basic principle, this method is capable of preparing a variety of semiconductor materials such as transition metals, post-transition metals, and rare earth metal oxides, which are worth further exploration. In addition, the use of low melting point liquid metal alloys also allows the method to be extended to other high melting point metals. Second, high-quality, large-area single-crystal semiconductor materials are necessary to meet the crystal quality requirements of electronic devices and for applications in high density semiconductor devices and integrated circuits, and to facilitate their practical application in industry. Liquid metals have the ability of liquid-solid phase transition to form large single crystal sheets with specific crystal orientation and can be used as growth substrates in the CVD process to achieve this goal step by step. On the other hand, amorphous liquid metals can be adopted as substrates to overcome the limitation of substrate symmetry. In addition, the obtained semiconductor single crystals can be used as substrates to grow single crystals by interlayer coupling to form multilayer two-dimensional (2D) semiconductor single crystals or vertical heterostructures. One of the remaining challenges in liquid metal semiconductor manufacturing is the assembly of such semiconductor structures into 2D heterostructures, which have a great potential for applications in making functional devices and deserve further exploration. Using van der Waals (vdW) stacking techniques and combining them with dry transfer, different types of heterojunctions of 2D semiconductors and other 2D materials can be realized. Liquid metals are highly metallically active and conductive, and therefore suitable for electrochemical redox processes on their surfaces. The reactions on the surface of liquid metals can be designed with precursors containing such metals. These precursors are then carried to the surface of the liquid metal so that the designed chemical interactions can produce ultrathin 2D semiconductor sheets on its surface. However, the development in this area is still in its infancy and it is possible to fabricate 2D semiconductors built from more metals by designing appropriate electrocouple substitution reactions on the surface of liquid metals.

In the near future, 2D semiconductors composed of more metals can also be fabricated by designing appropriate energy coupling substitution reactions on liquid metal surfaces. vdW stripping techniques can be used to tailor and assemble these homogeneous 2D semiconductor single molecule films at the atomic level, which may lead to the fabrication of superlattices and heterostructures. Liquid substrates offer ultra-fast, clean, and highly controllable sliding transport strategies. By integrating existing liquid metal-based floating flat glass technologies, controlled transfer of large areas of high-quality 2D semiconductors on liquid metal surfaces can be achieved and is expected to play a key role in future industrial manufacturing.

In summary, the newly emerging liquid metal printed semiconductors opens a promising avenue for quickly molding the next generation electronics, functional devices and even integrated circuits as well as user end chips. It will give new impetus to the semiconductor manufacture industry. Although the third generation semiconductor still cannot replace silicon materials at the current stage, as the family of liquid metal printed semiconductor materials continues to expand, more new semiconductor materials are expected to be developed, providing the basis for broader researches and applications, which are expected to lead to great industrial changes based on semiconductor material innovation and revolutionizing the energy fields such as low cost and green manufacture, solar decomposition of water for hydrogen production, photovoltaic power generation, wind power generation systems, electric and hybrid vehicles, etc.

References

1. Li Q, Du B D, Gao J Y, et al. Room-temperature printing of ultrathin quasi-2D GaN semiconductor via liquid metal gallium surface confined nitridation reaction. Advanced Materials Technologies, 2022, online, https://doi.org/10.1002/admt.202200733
2. Zhang Q, Zheng Y, Liu J. Direct writing of electronics based on alloy and metal (DREAM) ink: a newly emerging area and its impact on energy, environment and health sciences. Frontiers in Energy, 2012, 6(4): 311–340
3. Liu J, Wang Q. Liquid Metal Printed Electronics. Shanghai: Shanghai Science & Technology Press, 2019 (in Chinese)
4. Gao Y X, Li H Y, Liu J. Direct writing of flexible electronics through room temperature liquid metal ink. PLoS One, 2012, 7(9): e45485
5. Gao Y X, Liu J. Gallium-based thermal interface material with high compliance and wettability. Applied Physics. A, Materials Science & Processing, 2012, 107(3): 701–708
6. Lin J, Li Q, Liu T Y, et al. Printing of quasi 2D semiconducting β-Ga_2O_3 in constructing electronic devices via room temperature liquid metal oxide skin. Physica Status Solidi. Rapid Research Letters, 2019, 13(9): 1900271

7. Cooke J, Ghadbeigi L, Sun R J, et al. Synthesis and characterization of large-area nanometer-thin β-Ga_2O_3 films from oxide printing of liquid metal gallium. Physica Status Solidi. A, Applications and Materials Science, 2020, 217(10): 1901007
8. Messalea K A, Carey B J, Jannat A, et al. Bi_2O_3 monolayers from elemental liquid bismuth. Nanoscale, 2018, 10(33): 15615–15623
9. Li Q, Lin J, Liu T Y, Zhu X Y, et al. Gas-mediated liquid metal printing toward large-scale 2D semiconductors and ultraviolet photodetector. npj 2D Materials and Applications, 2021, 5: 36
10. Yuan T B, Hu Z, Zhao Y X, et al. Two-dimensional amorphous SnO_x from liquid metal: mass production, phase transfer, and electrocatalytic CO_2 reduction toward formic acid. Nano Letters, 2020, 20(4): 2916–2922
11. Syed N, Zavabeti A, Ou J Z, et al. Printing two-dimensional gallium phosphate out of liquid metal. Nature Communications, 2018, 9(1): 3618
12. Chen Y X, Liu K L, Liu J X, et al. Growth of 2D GaN single crystals on liquid metals. Journal of the American Chemical Society, 2018, 140(48): 16392–16395
13. Carey B J, Ou J Z, Clark R M, et al. Wafer-scale two-dimensional semiconductors from printed oxide skin of liquid metals. Nature Communications, 2017, 8(1): 14482
14. Alsaif M Y A, Pillai N, Kuriakose S, et al. Atomically thin Ga_2S_3 from skin of liquid metals for electrical, optical, and sensing applications. ACS Applied Nano Materials, 2019, 2(7): 4665–4672
15. Wang L, Liu J. Liquid metal material genome: initiation of a new research track towards discovery of advanced energy materials. Frontiers in Energy, 2013, 7(3): 317–332
16. Wei C, Fei H, Tian Y, et al. Isotropic Li nucleation and growth achieved by an amorphous liquid metal nucleation seed on MXene framework for dendrite-free Li metal anode. Energy Storage Materials, 2020, 26: 223–233
17. Liu J. Printable semiconductive device and its fabrication method. China Patent, 2012103572802, 2012 (in Chinese)