

Direct patterning of nanostructured ceramics from solution—differences from conventional printing and lithographic methods

Masahiro Yoshimura · Ruwan Gallage

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Abstract We have proposed an innovative concept and technology, “soft processing” or “soft solution processing,” which aims at low energetic (environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials by chemical reactions in or from solutions. By activating or stimulating those reactions locally and/or moving the reaction point dynamically, we can obtain patterned ceramic films directly in solution without any postheating, masking, or etching. Using those “direct patterning” concepts and technologies, we have developed methods for direct patterning of CdS, PbS, and CaWO₄ on paper substrates by *ink-jet reaction* at RT and TiO₂ patterning on a glass substrate by *ink-jet deposition* at <573 K. Furthermore, we have succeeded in fabricating a BaTiO₃ pattern by a laser beam-assisted process and a carbon pattern by a needle electrode, directly in solutions at ambient temperatures and pressures.

Keywords Pattern · Ceramic · Film · Solution · Soft chemistry · Ink-jet

Introduction

Numerous materials have been prepared in the form of thin and thick films and/or patterns over a century because of

the potential technical value of and scientific curiosity about their properties. A number of techniques have been investigated by searching for the most reliable and low cost methods of producing the films or patterns. The methods employed for ceramic film deposition can be divided into two groups based on the nature of the deposition process as physical methods (physical vapor deposition (PVD), laser ablation, sputtering, etc.) and chemical methods. The chemical methods comprise the gas phase deposition (chemical vapor deposition (CVD), atomic layer epitaxy, etc.) and liquid (solution-based) phase deposition such as spray deposition [1], sol-gel [2], spin coating [3], dip coating [4], etc. Those solution-based deposition methods have been called chemical solution deposition (CSD) [5]. Deki et al. [6] have developed another method, liquid phase deposition (LPD), to deposit ceramic films from or in solution.

In general, vacuum methods such as PVD, sputtering, and gas methods such as CVD, etc., use highly energetic species such as atoms, ions, and/or molecules as well as sophisticated instruments and high quality precursors; thus, they consume tremendous energy and exhaust huge amounts of gaseous wastes. Therefore, solution-based (liquid phase) deposition methods are becoming popular for the preparation of thin and thick films due to the low temperature process in a non-vacuum environment, easy control of the processing parameters, less energy consumption, hence, low cost methods, etc. The synthesis of ceramics from solution has also been encouraged by the development of environmentally friendly chemistry such as green and sustainable chemistry [7], soft chemistry (chimie douce) [8], and bio-inspired material chemistry [9]. The films obtained by those chemical methods including “sol-gel” methods using synthesized nanoparticles (powders) have generally been subjected to heating such as the post-

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M. Yoshimura (✉) · R. Gallage
Materials and Structures Laboratory,
Tokyo Institute of Technology,
4259 Nagatsuta,
Midori, Yokohama, Japan
e-mail: yoshimura@msl.titech.ac.jp

firing to consolidate them. Those heat treatments would cause cracking and/or peeling of the film due to the shrinkage by sintering of the particles or enhancing the grain growth and consequently would degrade the properties of the nanostructured films.

Furthermore, for applications in industrial electronic devices, those films have to be patterned. Many kinds of lithography have been developed to produce patterning, such as X-ray lithography [10], electron beam lithography [11], photolithography [12], etc. However, etching or lift-off processes are required in many of these methods, which increase the additional energy and materials consumption and make the processes complicated. The patterning process of films by the photolithography technique using masking has been regarded as essential to fabricate the present electronic or optical devices [13]. Although photolithographic technology is excellent for fabricating submicron-sized devices, and the applications for it are still expanding, it has an inherent shortcoming such as time consumption and a complex multi-step production process. Moreover, the subsequent photolithographic process removes the greater part of the film (some times exceeding 90%), and the supplemental materials in the photolithography process, such as photoresists, are also inefficiently used. The fabrication processes, shape forming and shape fixing mostly by sintering of powders at high temperature, would consume more energy than the synthetic processes for ceramic materials. Therefore, direct fabrication methods of nanostructured materials from precursors (not from a particle suspension) without multi-step post treatments such as masking, etching, post-firing, etc., will open a new way for fabrication of industrial electronic optical devices. Yoshimura et al. [14–16] proposed a novel concept and technology: soft processing or soft solution processing to fabricate ceramic materials with the desired shape, size, location, and orientation from aqueous solutions directly

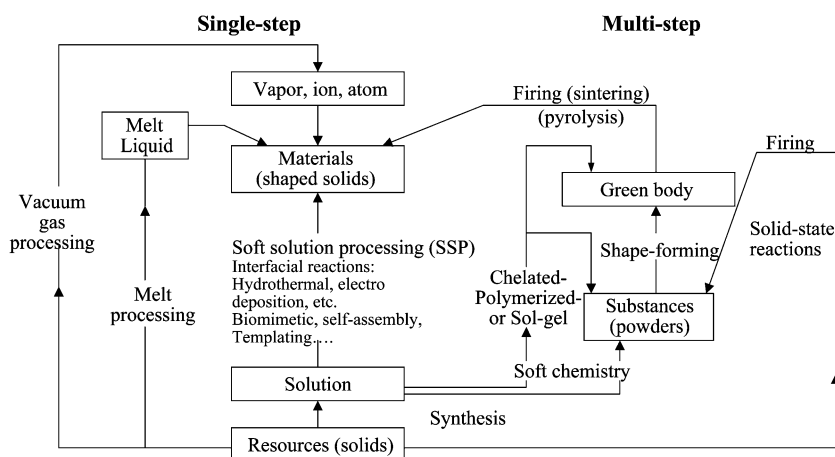
without post-firing and/or sintering of particles and/or powders after their shape forming (Fig. 1). In the present paper, we would like to propose and review the direct fabrication process introduced by our group using precursor solutions for preparing crystalline nanostructured thin film patterns (nanostructured materials) without any post-firing.

Thermodynamic aspects of ceramics fabrication

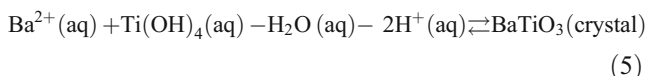
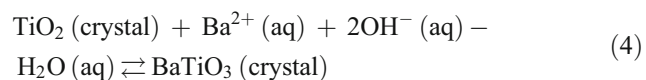
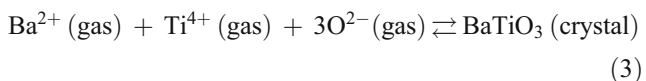
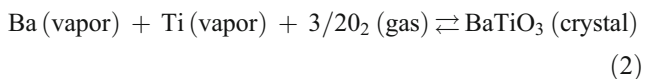
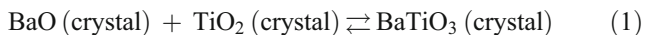
It is very difficult to produce ceramics with a desired shape and size directly (single step) due to their intrinsic brittleness. Thus, most of the ceramics have been fabricated via two-step processes using powders as shown in Fig. 1. These “traditional” and “classical” multi-step powder-processing methods have the merit of fabricating relatively large scale materials rather easily from powders as solid segments but also have demerits usually because they require high temperature treatments and consume a lot of energy. More recent processing routes using a gaseous phase and physical vapor deposition (PVD) methods in a vacuum system can produce shaped material in a single step but require even higher energy than standard high-temperature ceramic processes because gaseous species are in a much higher energetic state than solids as described below. Generally speaking, all of these gaseous methods have resulted in environmental problems because most of their consumed energy results in exhaust gas(es) or on exhaust heat (entropy) during the production of solid ceramic materials. Vacuum systems especially seem to put more stress on the environment because they require continuous pumping to maintain a vacuum, and their exhaust gas(es) cannot be recycled due to their large dilute volumes.

This can be demonstrated by synthesis reactions of BaTiO_3 using different phases of precursors. The driving forces (ΔG) for the representative syntheses reactions (1–5)

Fig. 1 Schematic diagram of advanced materials processes showing the flow of single-step and multi-step processes



of BaTiO₃ at 298 K as shown below are 159, 3,042, 15,418, 71, and -59 KJ/mol, respectively [16–18].



Any processing technique involving a gas–vapor phase requires a huge amount of energy (3,042–15,418 KJ/mol) to create these gas–vapor precursors from solid raw materials, which are oxide or carbonate ores, and this energy must then be released into the environment when solid BaTiO₃ is formed from these precursors. On the other hand, because the lattice energy of BaO and TiO₂ can be

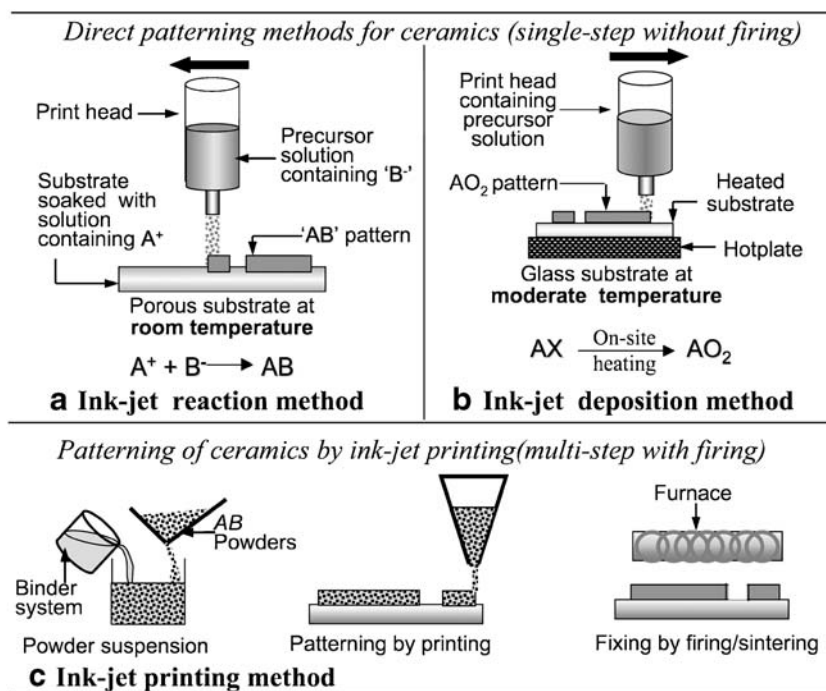
compensated for by the hydration (solvation) energies of Ba²⁺ and Ti⁴⁺ ions in solution, solution processing consumes very little energy if the activation energy (ΔG^*) for the synthesis can be overcome. Generally speaking, ΔG^* is inversely proportional to (ΔG^{-n}) , where $n=2$ for a homogeneous nucleation process. The gaseous species are always in high-energy states; thus, there is sufficient energy (ΔG) for the reaction to yield crystalline compounds with a desired shape or size. On the other hand, species in aqueous solutions are hydrated (or chelated by some complexing agents); thus, they are stabilized by the hydration (or chelation) energies and have only a small ΔG for the reaction. In those cases, relatively high activation energies are necessary for the reaction to occur by defeating those hydration (chelation) energies of the ions. Therefore, some particular interfacial reactions or activation processes, such as electro-, photo-, sono-, complexo-, organo-, or mechano-activation are required to accelerate the kinetics for synthesizing the crystallized single or multi-component ceramic materials from the solution.

Direct patterning of ceramic film by solution processing

Application of ink-jet technology

Ink-jet technology was originally developed as a contactless printing method, and it was used mainly for personal printings, commercial printings, data labeling of foodstuffs,

Fig. 2 Comparison of direct patterning of ceramics by **a** ink-jet reaction method, **b** ink-jet deposition method, and **c** conventional ink-jet printing of ceramics



etc. Now, it has been developed for applications in various fields such as electronic manufacturing (capacitors, semiconductors, dielectrics, functionally graded material, etc.) [19–23], photonics (lens arrays, display materials, wave guides, etc.) [24–26], medical diagnostics (immuno and DNA diagnostics, drug discovery, etc.) [27, 28], and combinatorial chemistry [29, 30]. The ink-jet technique for ceramic fabrication is believed to have many advantages such as simple devices, low cost and facile fabrication process, ease of mass fabrication, less materials waste, and the possibility of full automation and computer-control, thus, allowing for convenient control of the exact size and shape of such target devices. Initial work by Sachs et al. [31] did not directly print powder suspensions but instead printed a solution of binder materials onto a flat bed of metal or ceramic powder. Evans and co-workers [22] then initiated the ink-jet printing of ceramics from a slurry or suspension called a “ceramic ink.”

During the last decade, ink-jet printing has already been widely used for the fabrication of ceramic films, patterns, and three-dimensional (3D) structures using an ink, which is a suspension of ceramic particles in an organic solvent (colloidal fluid) [20, 32–37]. During ink-jet printing, these particles in the suspension are arranged into the required shape on the substrate, but there is no driving force to consolidate these particles and/or to fix the particles to the substrate except for their surface energy; thus, a heat

treatment at a high temperature is essentially needed for sintering [32, 38]. Therefore, only heat-resistant substrates can be used for those ink-jet printing methods. Furthermore, heat treatment at high temperatures can cause grain growth that affects the final properties of the film (e.g., electro-optical properties), contamination of the film due to the series of reactions that occur between the printed ceramic particles and the chemical species of the substrate at high temperature, etc. [22, 39, 40]. In order to minimize these drawbacks in the ink-jet printing methods, we have developed novel methods called *ink-jet reaction* and *ink-jet deposition* which are different from the conventional ink-jet printing of ceramic particles or powders as shown in Fig. 2. In our methods, an aqueous precursor solution is used instead of a colloidal ink for direct fabrication of a patterned ceramic film at room temperature or moderate temperatures without any further heat treatments.

Ink-jet reaction method

The ink-jet technique with a simple precipitation reaction of two chemical components can be used to fabricate ceramics patterns in a single step at room temperature (Fig. 2a). The ink-jet technique is employed to generate droplets which contain chemical species B^- , according to the desired pattern towards a substrate that contains the chemical species A^+ . When the droplets hit the substrate, the two

Fig. 3 Direct fabrication of CaWO_4 patterns by ink-jet reaction method. **a** Laser microscopic image of letters “IN”, **b** and **c** SEM images, and **d** XRD pattern

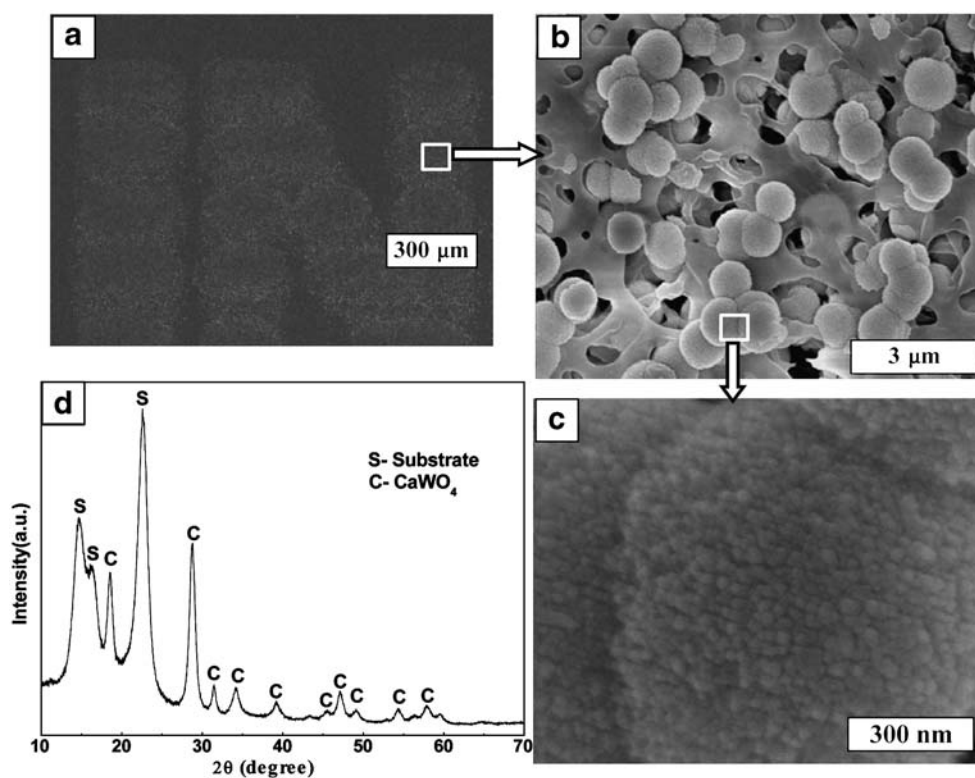
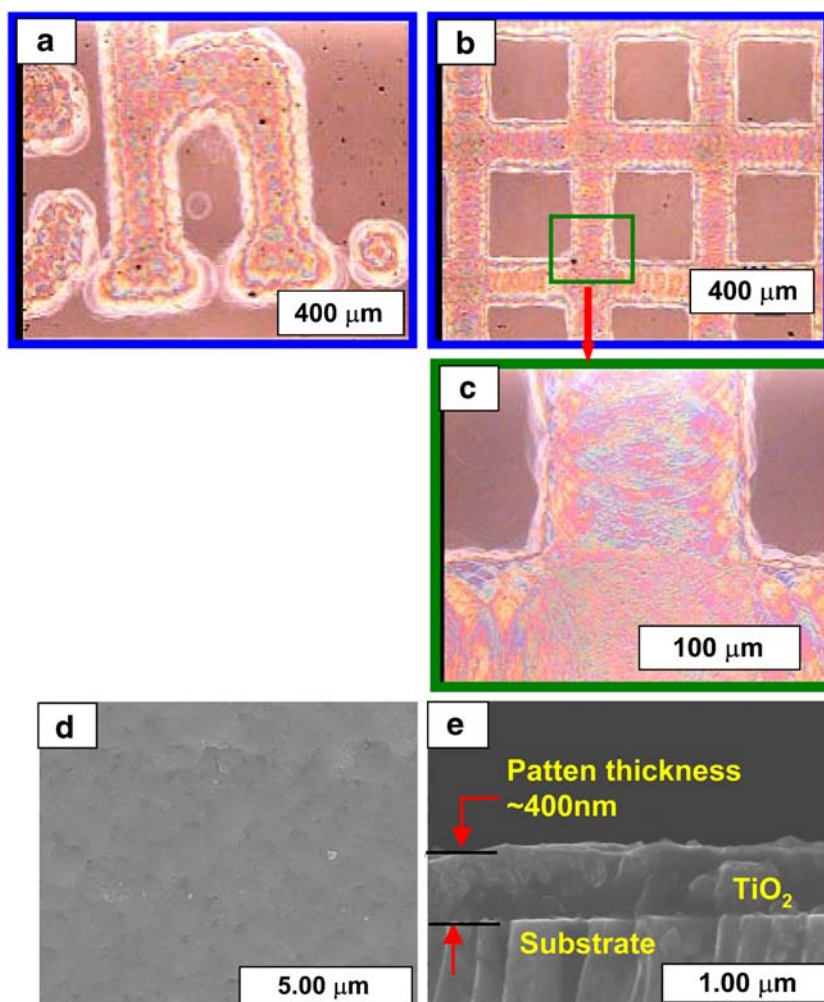


Fig. 4 Laser microscopic images (a, b, and c) and SEM images (d and e) of the patterned TiO₂ thin film by ink-jet deposition at 548 K



species react and form the AB compound on-site. The chemical driving force of the reaction $A^+ + B^- \rightleftharpoons AB$ can be used to synthesize the AB compound, and their consolidation or crystallization into a patterned AB can be produced with no postheating or mask and etching. This direct patterning using the ink-jet reaction is developed rather than the conventional ink-jet printing method where an ink containing AB particles has been jetted onto a substrate [35, 37]. This method is also applicable when both the chemical species of A and/or B can be dissolved in different ink solutions; the two inks can then be jetted onto a substrate. The ink-jet reaction method [41, 42] was successfully applied to fabricate patterns of sulfides (CdS, PbS) [41] and CaWO₄ [42] directly at room temperature. Figure 3 shows the patterned CaWO₄ on a mixed cellulose ester membrane filter by this method, which consists of consolidated nano-sized (15–35 nm) CaWO₄ crystals. On-site nucleation, growth, and consolidation of the compound (e.g., CdS, CaWO₄, etc.) also enhance the adhesion of the pattern to the substrate.

Ink-jet deposition method

As a development of the *ink-jet reaction* methods, we have introduced an *ink-jet deposition* methods [43, 44] for direct patterning of ceramics at an elevated temperature on a glass substrate using precursor solutions. In this single-step *ink-jet deposition*, the precursor solution is jetted towards the heated substrate according to the desired patterns (Fig. 2b) to form a crystalline pattern on-site. Therefore, postheat treatments are not required in contrast to the conventional ink-jet printings. In the *ink-jet deposition* method due to the decomposition of the precursor, nucleation, growth, and consolidation of oxide particles successively occur on the substrate or the already-deposited layer at moderate temperatures. Hence, crystalline patterns can be directly fabricated on-site without any post-firing and post treatments such as masking, etching, etc. Using the *ink-jet deposition* method, we have succeeded in preparing different shapes of TiO₂ patterns on glass substrates at 548 K using titanium tetraisopropoxide in ethanol and water as the precursor

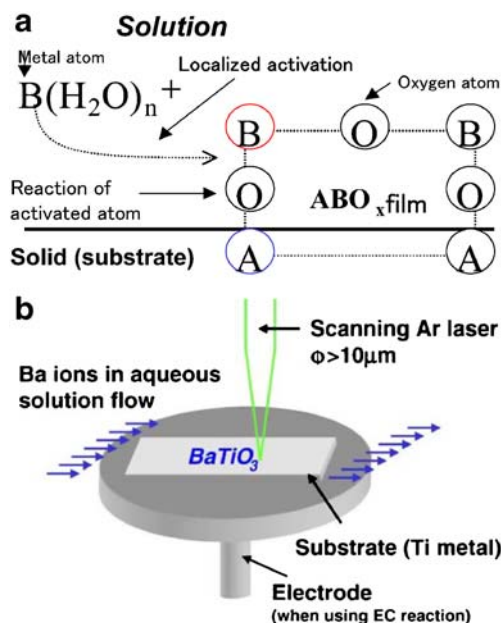


Fig. 5 **a** Concept of direct fabrication of double oxide ABO_x by the interfacial reaction between a substrate species (A) and a solute species (B) with a local activation and **b** the schematic diagram of the laser activation direct patterning in a flow system

solution [43]. As shown in Fig. 4, the width and thickness of the fabricated net shape pattern are ~ 120 and ~ 400 nm, respectively, without any cracks. The prepared patterns consisted of a nano-sized TiO_2 (anatase) phase and showed good adherence. We are now applying this method for thin film patterns of other materials such as CeO_2 [44]. This method requires appropriate solvents which prepare stable precursor solutions then vaporize and precipitate at the surface of the heated substrate. The successive decomposi-

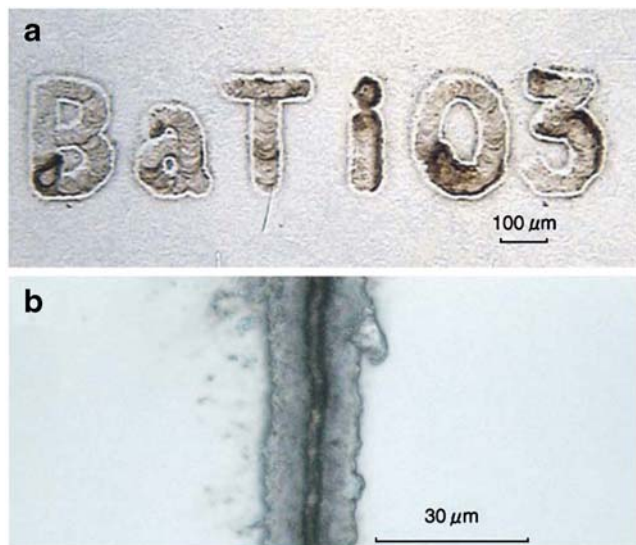


Fig. 6 Laser microscope images of **a** the fabricated $BaTiO_3$ pattern on a titanium substrate in $Ba(OH)_2$ solution and **b** the fabricated TiO_2 pattern on a silicon wafer in a titanium-containing complex solution by laser beam drawing

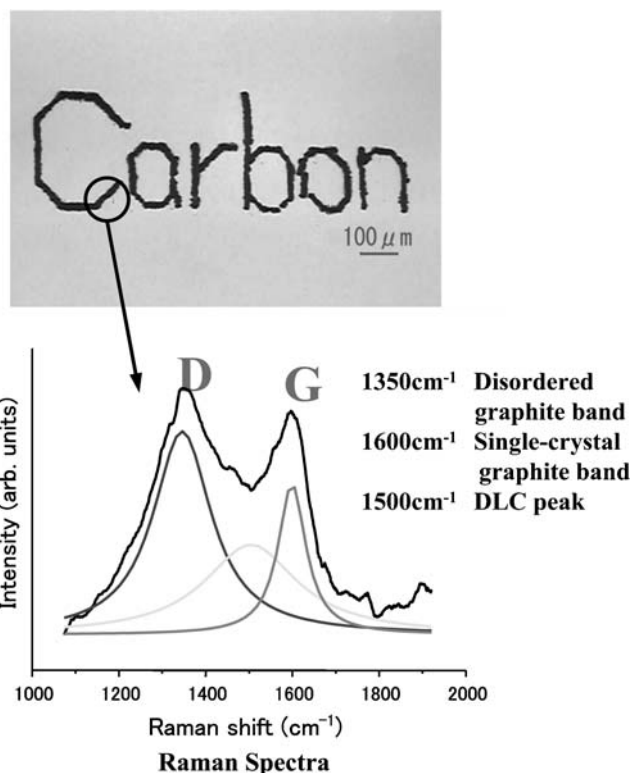


Fig. 7 Microscope image and Raman spectra of the patterned carbon film on a silicon substrate in ethanol

tion of the precursor could form the oxide pattern. The patterning of double oxides such as $BaTiO_3$ needs higher temperatures of about >873 K to crystallize, which is almost the same temperature use as the sol-gel film formations because the crystallization of the double oxide requires such high temperatures.

This ink-jet deposition method has a great merit of the continuous production of films even with desired patterns because the formation of the crystalline film is continuous on the heated substrate. This contrasts with conventional sol-gel methods where repeated batch processes, dip-spin coating \rightarrow drying \rightarrow firing \rightarrow cooling, are required. Recently, spin-spray deposition methods have been developed for the continuous deposition of ferrite films on a heated substrate (≈ 363 K) [45]. This method, however, has a disadvantage of a high wasting ratio of precursor solutions during spin-spraying.

Application of laser beam for direct patterning

Laser-assisted fabrication processes for preparing patterns (laser direct-write processing) have been used in various industrial applications due to the comparatively high speed, high precision processes, and the use of fewer chemicals and fewer process steps compared to the conventional semiconductor processing based on photolithography. C.B. Arnold et al. [46] have categorized these processes into

three main classes: laser direct-write subtraction, where material is removed by ablation [47]; laser direct-write modification, where material is modified to produce a desired effect [48]; and laser direct-write addition, where material is added by the laser [49]. Those laser-assisted methods consume large amounts of power to melt, vaporize, or modify the target materials.

However, the laser beam that was used for most of the processing techniques mentioned above was used for melting part of the substance or modifying the structure of the target material. However, we found that a focused laser beam could be effectively used to fabricate ceramic patterns directly on a substrate that was immersed in an aqueous solution by activating the interfacial reaction between species of the solid and the solution [50]. This is the novelty of the direct patterning of ceramics that we have introduced by the combination of the laser activation technique with a solution process (Fig. 5). Using this technique, a pattern of crystalline BaTiO₃ on a Ti substrate and a TiO₂ pattern on a SiO₂ substrate have been successfully fabricated at room temperature without any postheat treatments, as shown in Fig. 6. Nano-sized patterning by this method seems to be difficult because the laser beam heating cannot be concentrated in a nano-sized area, particularly in a solution.

Application of micro-discharge for direct patterning

Among the research on fabrication of ceramic films, radio frequency power has been applied mainly for sputtering a target material; hence, a highly energetic species (gas phase) is utilized under a vacuum condition [51, 52]. We have successfully used a micro-discharge using a radio frequency power supply between two electrodes in an organic solvent at room temperature and pressure for direct fabrication of patterned materials without any pretreatment or posttreatment [53]. By employing this method, patterning of amorphous carbon on a silicon wafer was successful in an ethanol solution using a tungsten wire (as a pen) and a silicon (111) wafer (substrate) as electrodes as shown in Fig. 7. The pattern, whose line width was about 20–30 μm, tightly adhered to the substrate without any posttreatment. It is proposed that, when electrolysis of a solvent is carried out using a thin wire electrode, local Joule heating occurs in the solvent. Under suitable conditions of energy dissipation, an arc discharge might be formed if the applied radio frequency voltage is sufficiently high. In this case, a very shallow primary reaction zone containing a high concentration of radicals originating from the organic solvent can be formed. Therefore, this method can produce an extreme environment that is closely analogous to those produced by plasma or ionizing radiation [54] but in an organic liquid under mild conditions such as ambient temperature and pressure.

Conclusions

We have succeeded in preparing various nanostructured ceramic thin film patterns directly in or from solution(s) without post-firing. The “direct patterning” of ceramics, where interfacial chemical driving forces have mostly been utilized for synthesis, shape forming and shape fixing rather than heat, thermal activation, in conventional ceramic processing, is contrasted to the conventional ceramic patterning methods, where multi-steps are required: (1) synthesis of particles of compounds or precursors, (2) dispersion of the particles into a liquid as an “ink,” (3) patterning of the particles on a substrate by printing of the “ink,” (4) consolidation and/or fixing the particles or pattern by firing. Individual methods described herein are original but are still in primitive stages and, thus, should be further developed in the future.

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