Soft Processing for Ceramics: Single-Step Fabrication of Nano-Structured Oxide Ceramics(Particles,Films,Integrated Layers and Patterns) from Solution without Firing

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Since 1989 when we found a method to fabricate BaTiO3 film on Ti substrate in a Ba(OH)2 solution by Hydrothermal Electrochemical[HEC] methodat low temperatures of 60-200□, we have proposed an innovative concept and technology, "Soft Processing" or "Soft Solution Processing," which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing.1,2) When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any firing, masking or etching. Those Direct Patterning methods differ from previous patterning methods which consist of multi-step processes, for example: (1) synthesis of particles of compounds or precursors,[When this synthesis is done in a solution it is called"Soft Chemistry".]
(2) dispersion of the particles into a liquid ("ink"), (3) patterning of the particles on a substrate by printing of the "ink", (4) consolidation and/or fixing of the particles' pattern by heating and/or firing at high temperatures. (5) Those processes would cause cracking and/or peeling of patterned films due to the shrincage of printed powders by sintering during heating and/or firing.
The notable feature of Direct Patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction, A+B=AB, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of firing is mostly used for the consolidation of the particles.3)
We have developed the Direct Patterning of CdS, PbS, and CaWO4 on papers by ink-jet reaction method and LiCoO2 by electrochemically activated interfacial reactions.4) Furthermore, we have succeeded to fabricate BaTiO3 patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions.5) Recent success in TiO2 and CeO2 patterns by Ink-jet deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300□, will be presented.6) Transparent films of several hundred nm thick can be oftained by 20 times of ink-jet scanning during 15-30 min. [Fig. 1]
As a development of Hydrothermal Electrochemical[HEC] method,we have proposed a new strategy:" Growing Integration Layer[GIL] method",which can provide well-adhered integrated/graded layers: Titanate/TiOx/Ti or Titanate/TiOx/Ti-alloys and/or metallic glass(es) at RT-150 C in a solution. This [GIL] strategy can be applied for many areas of functional ceramics.7-9)
In addition,our recent results on size and shape controlled mono-dispersed nano-particles of CeO210),(Hf,Eu)O2-x11),Fe3O412),etc.[Fig. 2] will be presented. The importance of complex formation by chelating agents will be clarified in the comparison of conventional "Sol-Gel" methods with "Polymerizable Complex" methods,which we proposed in 1992, 13)

Fig. 1

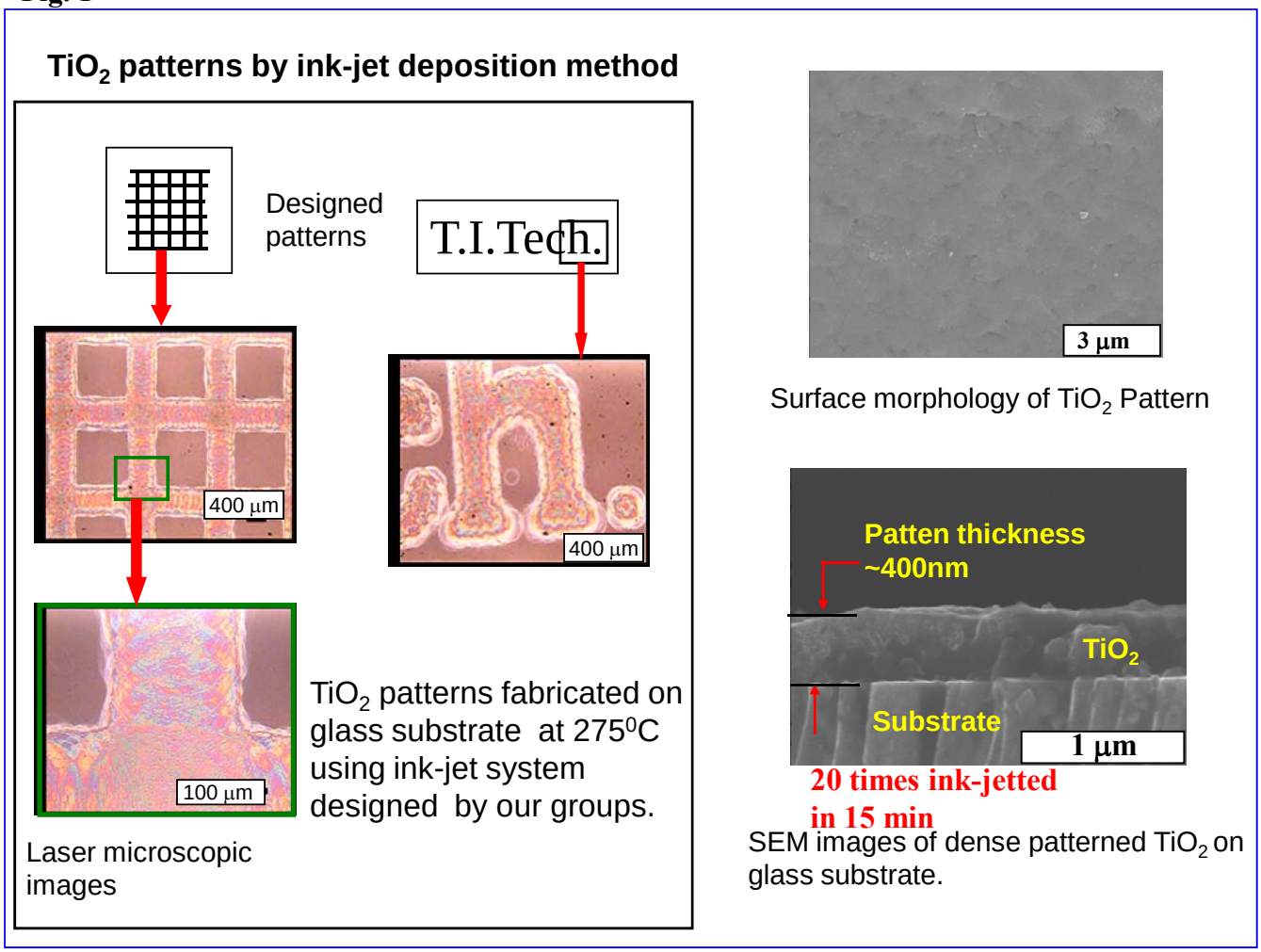
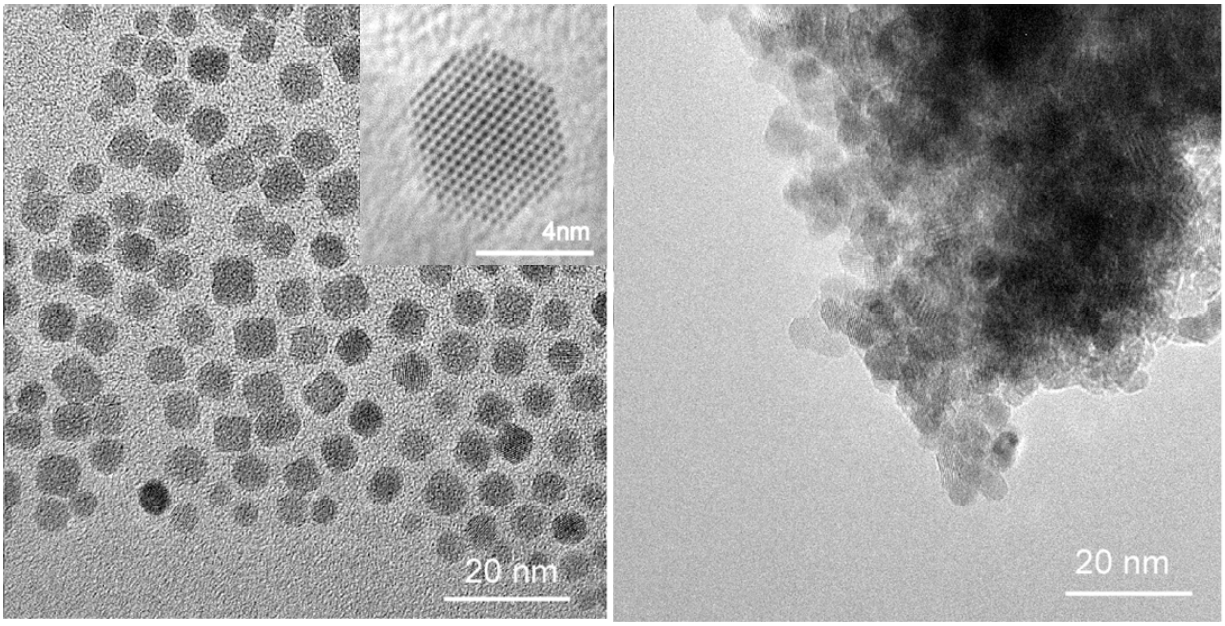

TiO2 patterns by ink-jet deposition method
Designed patterns
T.I.Tech.
400 μm
400 μm
100 μm
TiO2 patterns fabricated on glass substrate at 275⁰C using ink-jet system designed by our groups.
Laser microscopic images
3 μm
Surface morphology of TiO2 Pattern
Patten thickness ~400nm
TiO2
Substrate
1 μm
20 times ink-jetted in 15 min
SEM images of dense patterned TiO2 on glass substrate.

Fig.2

TEM observation of CeO_2 200℃, 6hours with oleate



With oleate

Without oleate

Taniguchi,Yoshimura et al., Cryst. Growth & Design,8(2008),3725

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