

# Size dependence of dislocation activities and independence on theoretical elastic strain limit in Pt nanocrystals revealed by atomic-resolution *in situ* investigation

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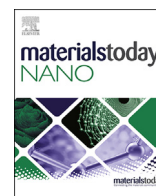
Nanocrystal

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## ABSTRACT

Because of the lower total number and density of defects in nanocrystals than those in their bulk counterparts, the elastic strain limits and the plastic deformation behaviors of the former can be very different from those of the latter. Furthermore, as the surface atomic ratio increases, a surface-dominant elastic and plastic deformation characteristic may appear in nanocrystal metals. The competition between nano-strengthening and surface effects thus determines the apparent mechanical behaviors of nanocrystal metals. In this study, we conducted a series of *in situ* atomic-resolution deformation experiments on high stacking fault energy platinum nanocrystals using an aberration-corrected high-

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# Nanomechanical characterization of titanium incorporated gallium oxide nanocrystalline thin films

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## ABSTRACT

The effect of titanium (Ti) incorporation on the crystal structure and mechanical properties of nanocrystalline gallium oxide ( $\text{Ga}_2\text{O}_3$ ) films (Ga-Ti-O) is reported. Ti content was varied from 0 to ~5 at% in the cosputter-deposited Ga-Ti-O films. The sputtering power applied to the Ti target was varied in the range of 0–100 W, while the sputtering power to  $\text{Ga}_2\text{O}_3$  was maintained at 100 W, to produce Ga-Ti-O films with variable Ti contents (0–5 at%). The Ti incorporation-induced effects were significant on the structural and mechanical properties. X-ray diffraction analysis indicated that structural transformation occurred with the increase in Ti content. The effect of Ti and associated microstructural changes are significant on the hardness (H) and elastic modulus ( $E_r$ ). The H values increased continuously from 25 to 30 GPa as a function of Ti up to 1.5 at%, after which a decreasing trend was observed. The Ga-Ti-O films exhibited excellent mechanical characteristics: H ~30 GPa,  $E_r$  ~310 GPa,  $H/E_r$  ~0.14, and  $H^3/E_r^2$  ~0.4 GPa, which are higher compared to those of intrinsic  $\beta$ - $\text{Ga}_2\text{O}_3$ . On the basis of these results, a structure-composition-mechanical property correlation in Ga-Ti-O films is established.

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## 1. Introduction

Gallium oxide ( $\text{Ga}_2\text{O}_3$ )-based thin films and nanomaterials have received considerable attention in recent years because of their wide range of technological applications in photonics, electronics, optoelectronics, magneto-electronics, chemical sensing, and catalysis [1–5]. Among the known wide band gap oxides, the scientific, technological merits, and potential of  $\text{Ga}_2\text{O}_3$  have been widely recognized [6–8].  $\text{Ga}_2\text{O}_3$  exhibits polymorphism; it can crystallize in five different crystal structures, namely  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  phases [9,10]. Among these polymorphs, monoclinic  $\beta$ - $\text{Ga}_2\text{O}_3$  is thermodynamically favorable and stable with a wide band gap of ~4.8 eV [9,10].  $\beta$ - $\text{Ga}_2\text{O}_3$  exhibits *n*-type conductivity related to donor centers involving oxygen vacancies and/or impurities [11–13]. The intrinsic  $\beta$ - $\text{Ga}_2\text{O}_3$  finds numerous technological applications in electronics, photonics, catalysis, electro-optics, gas sensing, deep ultraviolet (UV) photo electronics, and magnetoelectronics [14–17]. The thermal stability and higher melting point make  $\beta$ - $\text{Ga}_2\text{O}_3$  ideal for applications in extreme environmental conditions of high-temperature chemical sensors, catalysis, and thin-film transistors

[18–20]. However, the fundamental understanding of the physics and chemistry of  $\text{Ga}_2\text{O}_3$ -based nanomaterials is important for all the aforementioned applications. Such fundamental studies and understanding will allow the optimization of synthetic processes and conditions to provide a better control on the interplay among surface/interface structure, thermodynamic conditions, chemical processes, and kinetics, which in turn can facilitate the control of their properties and performance.

The goal of the present work is to design novel materials by selectively doping mechanically resilient Ti into Ga oxide (GTO) for extreme environment applications, such as high-temperature sensors, combustion systems, and photodetectors. The impetus for the present work is to derive a fundamental understanding of the nanomechanical behavior of GTO films with variable Ti contents and the effect of Ti on the structural and mechanical properties. Under reduced dimensions, especially on transition from micro- to nanoscale, the materials' performance is closely related to their ultra-microstructure and phase composition, and it also depends on the mechanical characteristics. Therefore, a controlled phase and microstructure are extremely important to improve the desired properties of oxides for a given technological application [21].

In fact, designing new and advanced materials must combine the excellent structural and electronic properties, which are comparable to those of currently existing materials, along with

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# Ductility and plasticity of nanostructured metals: differences and issues

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## ABSTRACT

Ductility is one of the most important mechanical properties for metallic structural materials. It is measured as the elongation to failure of a sample during standard uniaxial tensile tests. This is problematic and often leads to gross overestimation for nanostructured metals, for which non-standard small samples are typically used. Uniform elongation is a better measure of ductility for small samples because they are less sensitive to sample size. By definition, ductility can be considered as tensile plasticity, but it is often confused with plasticity. In principle, ductility is largely governed by strain hardening rate, which is in turn significantly affected by microstructure, whereas plasticity is primarily controlled by crystal structure or the number of available slip systems to accommodate plastic deformation. In practice, ductility is important for preventing catastrophic failure of structural components during service, whereas plasticity is critical for shaping and forming metals into desired shape and geometry to make structural components. Nanostructured metals typically have high plasticity, but low ductility, due to their low strain hardening capability. Increasing strain hardening rate via modifying microstructure is the primary route to improving ductility.

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## 1. Introduction

Reasonable ductility (usually >5%, preferably >10%) is desired to prevent mechanical components or structures from catastrophic failure during service [1]. On the other hand, high strength is also desired so that a metallic structure/component can carry large load at low material weight. This is especially important for future transportation vehicles such as electrical cars, which need to be lightweight to improve their energy efficiency. However, a metallic material is either strong or ductile, but rarely both at the same time [2,3]. Coarse-grained (CG) metals usually have high ductility but low strength. Refining grains to the nanocrystalline regime in the last few decades has significantly increased strength, but this is often accompanied with the sacrifice of ductility [4]. The low ductility of nanostructured metals has been a major issue with their potential structural applications.

Ductility of nanostructured metals has been a hot research topic for over a decade [2–7]

# Nanospace within metal–organic frameworks for gas storage and separation

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## ABSTRACT

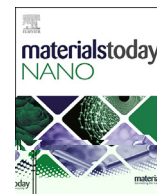
Porous metal–organic frameworks (MOFs), also known as porous coordination polymers, represent a

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# Indocyanine green–encapsulated nanoscale metal–organic frameworks for highly effective chemo-photothermal combination cancer therapy

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## ABSTRACT

Indocyanine green (ICG), as the only U.S. Food and Drug Administration–approved near-infrared (NIR) clinical agent, has been considered as an ideal light absorber for laser-mediated photothermal therapy (PTT) in cancer treatment. However, the practical applications of ICG are severely hampered by its poor aqueous stability, rapid body clearance, and low cellular uptake. To overcome these limitations, we herein report the successful example of integrating ICG into a zeolitic imidazolate framework (ZIF-8) to fabricate a novel nanoscale ICG@ZIF-8 hybrid material. Through a simple one-pot synthesis method, a high loading content of 20.6% can be achieved in the resultant ICG@ZIF-8. The photostability and tumor accumulation of ICG are notably promoted due to the protection of the framework, leading to enhanced photothermal conversion efficiency. Furthermore, we also discover, for the first time, that the pH-triggered release of large amount of  $\text{Zn}^{2+}$  from ZIF-8 in tumor acidic microenvironment also significantly contributes to targeted killing of cancer cells. As a result of the combined PTT and chemotherapy, ICG@ZIF-8 exhibits greatly improved diagnostic efficacy for both *in vitro* and *in vivo* cancer therapy, leading to 91% tumor eradication in all the mice treated with ICG@ZIF-8 and NIR irradiation. Hematoxylin and eosin (H&E)–stained slices show that no noticeable tissue damage is observed in major organs, indicating the safety of ICG@ZIF-8.

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## 1. Introduction

Photothermal therapy (PTT), which uses an optical absorbing agent to efficiently convert light energy into heat which causes a rise in the local temperature beyond 42°C to consequently kill cancer cells, has been widely recognized as a promising non-invasive strategy for future cancer treatment. Much effort has been dedicated to the development of near-infrared (NIR) laser (ranging from 700 to 1,100 nm)–assisted PTT because of its low tissue adsorption, deep penetration ability, and low phototoxicity [1–3]. Until now, a large number of NIR-adsorbing inorganic agents,

including gold nanostructures [4–7], carbon nanotubes [8–11], and copper sulfide nanoparticles (NPs) [12], have been extensively used as PTT agents. However, these inorganic agents are non-biodegradable and generally have potential long-term toxicity, which seriously limit their clinical applications. In this regard, indocyanine green (ICG), the only U.S. Food and Drug Administration–approved NIR agent, exhibits higher photothermal conversion efficiency and better biocompatibility [13]. However, ICG is not an effective PTT agent for practical applications because of its easy photodegradation, rapid blood clearance (an ultra-short half-life period of 2–4 min), and low tumor accumulation rate [14–16]. Therefore, the development of novel platforms to improve the photostability and tumor accumulation of ICG is urgently desirable for highly efficient PTT.

To overcome the aforementioned issues, various NP-based delivery systems, such as polyallylamine, perfluorocarbon, poly-peptide micelles, and poly (lactic-co-glycolic acid)–constituted

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# Advances in understanding atomic-scale deformation of small-sized face-centered cubic metals with *in situ* transmission electron microscopy

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## ABSTRACT

Face-centered cubic (fcc) metals exhibit outstanding mechanical properties both in small-sized and bulk nanostructures and are thus promising for applications in micro/nano electromechanical systems (M/NEMS). Uncovering the intrinsic deformation mechanisms of small-sized metals is of critical importance for evaluating their feasibility in M/NEMS applications. Recent advances in *in situ* transmission electron microscopy (TEM)-based mechanical testing techniques open up opportunities for achieving a mechanistic understanding of the atomic-scale deformation mechanisms. This article reviews recent progresses in *in situ* TEM studies on the various plastic deformation modes of small-sized fcc metals, including dislocation slip and twinning, phase transformation-mediated plasticity, reversible structure formation, diffusion-mediated plasticity, and void-assisted plasticity and fracture. Promising directions for future *in situ* TEM investigations on fcc metals are also enumerated.

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## 1. Introduction

The excellent mechanical performances of nanostructured materials generally originate from their unique deformation mechanisms [1,2]. Deformation modes of materials are known to be size and structure dependent [3,4]. Revealing the competition and interaction between different deformation modes is technically demanding yet critical for the design and process of advanced materials. Applications in the micro/nano electromechanical systems (M/NEMS) necessitate interrogating the mechanical properties of nanostructured materials at small scale (e.g. <50 nm in diameter) [5], which further increases the technical difficulties involved therein. To date, the understanding of atomistic deformation mechanisms has been highly dependent on computational simulations [6–9], the reliability of which can be affected by their inherent high strain rates (i.e.  $10^7$ – $10^9$ /s in computation vs.  $<10^{-1}$ /s in laboratory) and accuracy of the applied interatomic potentials. As a result, advanced experimental techniques capable of direct observation on the dynamic deformation process are highly appealing.

Recent advances in *in situ* mechanical testing techniques have been proved very effective in revealing the dynamic deformation processes of nanomaterials [10]. In particular, transmission electron microscopy (TEM)-based techniques [11–14] open up opportunities for achieving a fundamental understanding on the deformation mechanisms at micro or even atomic scale [15]. The small dimension of specimens used in *in situ* TEM studies are often comparable with those in computations [16], allowing good comparisons between the experimental and theoretical results. Most importantly, direct evidence demonstrated in *in situ* mechanical studies is typically beyond the reach of *ex situ* experimental methods and is thus critical for proving/disproving computational results and uncovering possible new deformation mechanisms. Being one of the most prevailing structures in metals, face-centered cubic (fcc) metals, such as copper alloys, aluminum alloys, and stainless steels, are extensively applied in the industry. Their prominent mechanical properties can be attributed to their tremendous deformation modes [17], which are complex and can often only be revealed by sophisticated investigation techniques. This article overviews recent *in situ* TEM studies on the plastic deformation in small-sized fcc metals and discusses the detailed deformation mechanisms from five aspects, including slip and twinning, phase transformation, reversible structures formation, surface diffusion-mediated deformation, and void-mediated

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