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Formation of Ti_2AuN from Au-covered Ti_2AlN thin films: A general strategy to thermally induce intercalation of noble metals into MAX phases

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KEYWORDS: MAX phase, nanolaminated structure, noble metal intercalation

ABSTRACT: Thermally-induced intercalation of noble metals into non-van der Waals ceramic compounds presents a method to produce a new class of layered materials. We recently demonstrated an exchange reaction of Au with A layers of MAX phase carbides with plentiful combinations of A and M elements. Here, we report the first substitution of Al with Au in a Ti_2AlN MAX phase nitride at an elevated temperature without destroying the original layered structure. These results bolster the generalization of the Au intercalation for the A elements in MAX phases with diverse combinations of M, A, and X elements. Furthermore, we propose crucial factors to achieve the exchange reaction: there should be a chemical potential for the A element to dissolve in or react with noble metals to intercalate; the noble metals should be inert to the initial metal

carbides/nitrides; and it is necessary to choose the reaction temperature that allows balanced interdiffusion of the noble metals and A elements.

$M_{n+1}AX_n$ phases ($n = 1, 2, \text{ or } 3$) are a set of endogenously nanolaminated ternary materials. In this polymorph, $M_{n+1}X_n$ slabs are structurally interleaved with A layers, where M is a transition metal, A is an element of groups 13-16, and X is carbon or nitrogen. This particular layered arrangement possesses advantageous chemical and physical properties, which combine characteristics of both metals and ceramics, such as resistance to thermal shock and high thermal and electrical conductivities^{1, 2}. Of particular interest in recent years are $M_{n+1}AX_n$ phases as a precursor to form a newly established class of two-dimensional materials, *MXenes*; appropriately opted etchants can exfoliate $M_{n+1}AX_n$ phases by selectively etching the A layers and leave laminated $M_{n+1}X_n$ terminated with T_n that stands for surface terminations such as hydroxide and fluorine^{3, 4}. There are various chemicals and methods used to etch away A elements⁵. The A elements of $M_{n+1}AX_n$ phases can also be removed by out-diffusion while reacting with surrounding materials. For example, Ti_3SiC_2 thin films are decomposed to amorphous TiC_x entailing out-diffusion of Si into deposited Cu⁶, Ni⁷, Al⁸, and molten cryolite⁹ at the elevated temperature; therefore, the original layered structures are ruined.

Exchange of the A layers would modify the properties of $M_{n+1}AX_n$ phases. We recently demonstrated replacement of Si as the A element in Ti_3SiC_2 with Au deposited on the top¹⁰, which was the pioneering intercalation of noble metals in non-van der Waals solids different to what was conventionally recognized for van der Waals solids¹¹⁻¹⁴. Contrary to the above materials forming intermetallic phase with Si that block the interdiffusion of the deposited materials into Ti_3SiC_2 , Au

forms metastable Au-Si silicides that might act as transport phases for interdiffusion of both Au and Si¹⁵⁻¹⁸. Accordingly, vacancies in the Si layer created by its out-diffusion can be simultaneously back-filled with Au atoms. The resulting Ti₃AuC₂ showed remarkable thermal stability and functioned as a stable ohmic electrical contact to a SiC substrate in harsh oxidizing environments. Starting with Ti₃SiC₂ as the model case, the substitutional intercalation of Au with A elements in M_{n+1}AX_n phases was achieved using T_{n+1}AlC_n (n = 1 and 2)¹⁹, Mo₂Ga_nC (n = 1 and 2)²⁰, and (Cr_{0.5}Mn_{0.5})₂GaC²¹ while the layered structures of these M_{n+1}AX_n phases remained in the resulting compounds. This suggests a generalization of the substitutional reaction for at least M_{n+1}AX_n phase carbides with a possible additional combination of M and A elements hitherto unexplored.

To clarify whether the substitutional intercalation of Au is comprehensively operational for M_{n+1}AX_n phases, the Au substitution reaction should be examined also for M_{n+1}AX_n phase nitrides (X = N), for which intercalation of noble metals has not been realized. Due to an additional valence electron in N compared to C and thus its larger electronegativity than C, nitrides and carbides are fundamentally different in terms of properties of their bonding²². Furthermore, MAX phase nitrides and carbides show distinct differences in the distribution of the density of states²³. Thus, the electronic and electrical conductivity/resistivity properties of MAX phases differ significantly between the two types of ceramics. Therefore, it is of importance to test the intercalation of Au into both MAX phases to establish any universality of the substitutional reaction. An attractive candidate for such attempts is Ti₂AlN owing to its superior electrical conductivity compared with Ti₂AlC of the carbide counterpart²⁴⁻²⁶ as Ti₃AlN₂ has not been realized²⁷. While the electrical conductivity of Ti₂AuN has not yet been possible to measure, due to the prevailing condition of retained unreacted Ti₂AlN parts, the intercalation of noble metals

into Ti_2AlN would be expected to enhance its thermal stability of relevance to electronic applications.

In that context, we here report on the formation of a new nanolaminated thin film of Ti_2AuN by replacing Al with Au in Ti_2AlN via thermally induced intercalation. This is the first time that the substitutional intercalation of Au in $\text{M}_{n+1}\text{AX}_n$ phase nitrides has been demonstrated. Furthermore, we discuss crucial factors for this phenomenon: sufficient solubility or reactivity of such noble metal with the original A element and stability of the M_{n+1}X_n sublayers against the noble metal incorporated into $\text{M}_{n+1}\text{AX}_n$ phases.

Ti_2AlN was grown on c-plane sapphire (001) substrates by using direct current magnetron sputter (DCMS) deposition from metallic targets of Ti and Al. The deposition was performed under a N_2/Ar mixture atmosphere at a total deposition pressure of 3 mTorr. The gas flow ratio of N_2/Ar was kept at 1/20. The applied power for Ti and Al targets was 300 and 100 W, respectively. The Al and Ti targets were placed to the substrate perpendicularly and at a 35° angle tilted off the substrate normal, respectively. The substrates were heated up to 1173 K prior to deposition at a rate of 30 K/min. The base pressure was kept at 10^{-8} Torr in the chamber. More details of the deposition system and the experimental approach may be found elsewhere²⁸.

The deposited Ti_2AlN thin films were etched in buffered HF (NH_3F (25 g) + H_2O (50 ml) + HF (10 ml)) for 5 s to remove residual oxides on the surface and immediately transferred into the other deposition chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The films were covered with Au to a thickness of 500 nm using DCMS from a Au target placed at 20 cm above the sample and 20° tilted away from the sample. The Au-covered samples were transferred into a quartz tube inserted in a tube furnace for annealing at 673 K for 5 h and subsequently at 773 K for 6 h. The

furnace was heated up at a ramping rate of ~ 18 K/min. To avoid oxidation of the samples, nitrogen gas was flowing through the quartz tube for 2 h before and during annealing.

The phase composition of the samples was identified from X-ray diffraction (XRD) patterns, acquired by a Philips PW 1820 diffractometer using Cu K α radiation. Scanning electron microscopy (SEM) was performed in a LEO 1550 for imaging and energy dispersive X-ray analysis (EDX) of the surface. Structural analysis was carried out by high-resolution STEM high angle annular dark field (HRSTEM-HAADF) imaging within Linköping's double C_s corrected FEI Titan³ 60-300 microscope operated at 300 kV. HRSTEM-HAADF imaging was performed using 21.5 mrad probe convergence angle. The corresponding cross-sectional samples were mechanically polished to a thickness of about 60 μm , followed by ion-beam milling with Ar⁺ in a Gatan precision ion polishing system at 5 keV with a final polishing step at 1 keV of ion energy.

We studied the surface and bulk composition of the Au-deposited Ti₂AlN film after annealing. Figure 1 shows the SEM/EDX analysis of the sample, where Al islands have formed on the Au surface. Al from the A layer separating Ti₂N was diffused out into the deposited Au layer similar to previously reported cases of the Au intercalation into other M_{n+1}AX_n phase carbides with A = Si, Al, and Ga^{10, 19-21}. Interdiffusion between Au and Al is active at our annealing temperature^{29, 30}. Moreover, Al atoms are loosely bonded to Ti in the Ti₂AlN crystal. Thus, in the presence of Au covering Al, the diffusion of Al into Au occurs as Al atoms have a lower chemical potential in an Au reservoir than in the Ti₂AlN crystal. As a result, at the appropriately selected temperature Al can more or less completely segregate to the surface through the top Au layer, as shown in Figure 1, without ruining the layered structure of the MAX phase. Figure 2 shows HRSTEM images of annealed Au-deposited Ti₂AlN acquired along the zone axes [11 $\bar{2}$ 0] and [1 $\bar{1}$ 00]. The brightness in the STEM is proportional to the mass of atoms through which a beam

of electrons is transmitted. The atomic arrangements correspond to those of a M_2AX phase: the typical laminar structure comprised of layers of a heavy element, Au, alternating Ti_2N layers. Each Ti_2N sheet is stacked on one another with a zig-zag pattern sandwiched by Au monolayers. This evidently means that out-diffusion of Al induced by the elevated temperature occurs with in-diffusion of Au without destroying the original layered structure.

Figure 1. The SEM image (left) and elemental mapping of the surface of annealed Au-deposited Ti_2AlN : Au (center) and Al (right).

Figure 2. HRSTEM images of annealed Au-covered Ti_2AlN acquired along the $[11\bar{2}0]$ (a) and $[1\bar{1}00]$ (b) zone axes. Yellow, grey, and red balls represent Au, Ti, and N atoms, respectively, revealing Ti_2AuN formation. Scale bars, 1 nm.

To get a deeper understanding of the crystal structure, we performed HRSTEM and XRD for the prepared samples. According to a line profile of the HRSTEM images analyzed by GMS3 software, the *c* lattice parameter expands upon the Al-Au exchange from 13.66³¹ to 14.05 Å. Figure 3 shows the XRD patterns for the samples before and after Au infusion. Diffraction peaks at about 13 and 26° correspond to (0002) and (0004) of Ti₂AlN, respectively. The peak appearing at about 28° after annealing is attributed to Al-Au intermetallic phases of AlAu₄ formed on top of samples due to diffusion of Al into Au as shown in Figure 1²⁹. It is known that at the elevated temperature, various intermetallic phases are formed as a result of interdiffusion between Au and Al: Al₂Au, AlAu, AlAu₂, Al₂Au₅, and AlAu₄³². Al₂Au₅ was found to be initially a predominant phase at 733 K close to our annealing temperature of 773 K. However, it was reported that unstable Al₂Au₅ rapidly transformed into AlAu₄ at a lower temperature of 673 K²⁹. In this work, Al₂Au₅, which would form at our annealing temperature, might be transformed into AlAu₄ during cooling. Therefore, the identical diffraction peak of Al₂Au₅ does not appear in Figure 3. The Au-exchange reaction resulted in slightly broadening (000*l*) peaks. This expansion would correspond to residuals of Ti₂AlN and Ti₂AuN. The MAX crystal structure is preserved during the Au-exchange reaction, where HRSTEM images reveal a lattice expansion by 2.9 % corresponding to a theoretical shift of the (0004) diffraction peak by 0.71°³³. Due to such a slight shift, the diffraction peaks of (000*l*) seem to get broadened after annealing; for example, for (0004) the original FWHM of 0.31° was increased by 0.35°. The overlapping peaks also imply that the A atom exchange was not completed for the duration of the annealing experiment as there is some retained Ti₂AlN phase. For the case of the intercalation of Au into Ti₃SiC₂, the substitution of Si with Au takes place from the top surface of Ti₃SiC₂ toward the substrate layer by layer¹⁰. We thus expect the substitutional reaction

occurs for Ti_2AuN in the same manner and annealing it longer, therefore, would complete the exchange.

Figure 3. XRD patterns of Au-covered Ti_2AlN before and after annealing.

These results verify the assumption that the replacement of Al with Au would be triggered by out-diffusion of Al along with simultaneous in-diffusion of Au, which compensates for the formed Al vacancies to preserve the original structure of the M_2AX phase nitride. Herein, we thus generalize the strategy to intercalate noble metals into $\text{M}_{n+1}\text{AX}_n$ phases by expanding the sets of combinations of M, A, and X elements. As proposed previously²⁰, the Au-exchange reaction takes

place between Au atoms capping the $M_{n+1}AX_n$ phase and original A atoms of the $M_{n+1}AX_n$ phase with the two-step process: (1) introducing vacancies in the A layers by diffusion of the A elements and (2) subsequent backfilling the vacancies with a new intercalated element, denoted as A'.

To trigger the massive replacement of A with A', A' has to introduce instability in the bonding of A adjacent to A' at the interface. There should be a chemical potential for the A element to dissolve in or react with noble metals; in addition, the MX layered structure has to be stable against the diffusion of both A and A' atoms through the layers. For example, at the annealing temperature of this work, TiN is stable in the presence of various metals surrounding TiN, including Au^{34, 35}, so that the intercalation of Au into Ti_2AlN introduces no transformation of the original layered structure. On the other hand, deposited Cu⁶, Ni⁷, Al⁸, and molten cryolite⁹ destroys the layered Ti_3C_2 or Ti_3SiC_2 into amorphous TiC_x at the elevated temperature; therefore, the intercalation of these elements is ruled out. This is opposed to Au, which causes no critical instability of the structure of Ti_3C_2 . In this work, Al and Au formed $AlAu_4$. However, due to the preponderance of gold-rich phases such as Al_2Au_5 and $AlAu_4$, the intermetallic layers are prone to grow into Au at the top interface³⁰. Thus, the balanced interdiffusion between Al and Au can take place without damaging the structure of the $M_{n+1}AX_n$ phase despite the formation of intermetallic phases. By aptly selecting the A-A' combination and annealing temperature, intercalation of A' into $M_{n+1}AX_n$ phases would be universally operational, where A' is not only limited to experimentally realized Au intercalation but also for other noble metals.

In conclusion, we demonstrate that thermally-induced intercalation of Au into Ti_2AlN can be used to form Ti_2AuN as a noble phase. We also discuss the mechanism of the exchange reaction of noble metals and A layers and propose key factors for the corresponding reaction. A' should exhibit negative heat of mixing with A at the annealing temperature; the layered structure of the

original $M_{n+1}AX_n$ should be stable against the exchanged elements; and the appropriate temperature of annealing has to be selected to meet all the above requirements. Our results bolster the generality of the intercalation process for $M_{n+1}AX_n$ phases to plentiful combinations of comprising M, A, and X elements. They also pave a strategy to explore the new class of layered transition metal carbides/nitrides with tailored chemical and physical properties. Furthermore, this strategy should be envisioned to intercalate noble metals into not only thin films of $M_{n+1}AX_n$ phases but also corresponding bulk or particulate $M_{n+1}AX_n$ phases.

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Author Contributions

S.K. and C.L. designed the experiments and analyzed the data. S.K. wrote the manuscript, with input from all co-authors. S.K., C.L., A.P., and J.L. performed the experiments. L.H. and J.R. supervised the project.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DCMS, direct current magnetron sputter; XRD, X-ray diffraction; SEM, Scanning electron microscopy; HRSTEM-HAADF, high-resolution scanning transmission electron microscopy high angle annular dark field.

REFERENCES

1. Barsoum, M. W., The $M_{N+1}AX_N$ phases: A new class of solids: Thermodynamically stable nanolaminates. *Prog. Solid State Chem.* **2000**, 28, 201-281.
2. Eklund, P.; Rosen, J.; Persson, P. O. Å., Layered ternary $M_{N+1}AX_N$ phases and their 2D derivative MXene: an overview from a thin-film perspective. *J. Phys. D: Appl. Phys.* **2017**, 50, 113001.
3. Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y., 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2017**, 2, 16098.
4. Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W., Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Adv. Mater.* **2011**, 23, 4248-4253.
5. Verger, L.; Natu, V.; Carey, M.; Barsoum, M. W., MXenes: An Introduction of Their Synthesis, Select Properties, and Applications. *Trends Chem.* **2019**, 1, 656-669.
6. Zhou, Y.; Gu, W., Chemical reaction and stability of Ti_3SiC_2 in Cu during high-temperature processing of Cu/ Ti_3SiC_2 composites. *Z. Metallkd.* **2004**, 95, 50-56.

7. Yin, X.; Li, M.; Zhou, Y., Microstructure and mechanical strength of diffusion-bonded $\text{Ti}_3\text{SiC}_2/\text{Ni}$ joints. *J. Mater. Res.* **2006**, *21*, 2415-2421.
8. El-Raghy, T.; Barsoum, M.; Sika, M., Reaction of Al with Ti_3SiC_2 in the 800–1000° C temperature range. *Mater. Sci. Eng., A* **2001**, *298*, 174-178.
9. Barsoum, M. W.; El-Raghy, T.; Farber, L.; Amer, M.; Christini, R.; Adams, A., The Topotactic Transformation of Ti_3SiC_2 into a Partially Ordered Cubic $\text{Ti}(\text{C}_{0.67}\text{Si}_{0.06})$ Phase by the Diffusion of Si into Molten Cryolite. *J. Electrochem. Soc.* **1999**, *146*, 3919-3923.
10. Fashandi, H.; Dahlgqvist, M.; Lu, J.; Palisaitis, J.; Simak, S. I.; Abrikosov, I. A.; Rosen, J.; Hultman, L.; Andersson, M.; Spetz, A. L., Synthesis of Ti_3AuC_2 , $\text{Ti}_3\text{Au}_2\text{C}_2$ and Ti_3IrC_2 by noble metal substitution reaction in Ti_3SiC_2 for high-temperature-stable Ohmic contacts to SiC. *Nat. Mater.* **2017**, *16*, 814.
11. Whittingham, M. S., Chemistry of intercalation compounds: metal guests in chalcogenide hosts. *Prog. Solid State Chem.* **1978**, *12*, 41-99.
12. Van der Ven, A.; Bhattacharya, J.; Belak, A. A., Understanding Li diffusion in Li-intercalation compounds. *Acc. Chem. Res.* **2012**, *46*, 1216-1225.
13. Koski, K. J.; Cha, J. J.; Reed, B. W.; Wessells, C. D.; Kong, D.; Cui, Y., High-density chemical intercalation of zero-valent copper into Bi_2Se_3 nanoribbons. *J. Am. Chem. Soc.* **2012**, *134*, 7584-7587.

14. Yao, J.; Koski, K. J.; Luo, W.; Cha, J. J.; Hu, L.; Kong, D.; Narasimhan, V. K.; Huo, K.; Cui, Y., Optical transmission enhancement through chemically tuned two-dimensional bismuth chalcogenide nanoplates. *Nat. Commun.* **2014**, *5*, 5670.
15. Tu, K., Selective growth of metal-rich silicide of near-noble metals. *Appl. Phys. Lett.* **1975**, *27*, 221-224.
16. Hiraki, A.; Lugujo, E.; Mayer, J. W., Formation of silicon oxide over gold layers on silicon substrates. *J. Appl. Phys.* **1972**, *43*, 3643-3649.
17. Lee, S.-H.; Stephens, J. A.; Hwang, G. S., On the nature and origin of Si surface segregation in amorphous AuSi alloys. *J. Phys. Chem. C* **2010**, *114*, 3037-3041.
18. Okamoto, H.; Massalski, T., The Au– Si (gold-silicon) system. *Bull. Alloy Phase Diagrams* **1983**, *4*, 190-198.
19. Fashandi, H.; Lai, C.-C.; Dahlqvist, M.; Lu, J.; Rosen, J.; Hultman, L.; Greczynski, G.; Andersson, M.; Spetz, A. L.; Eklund, P., $\text{Ti}_2\text{Au}_2\text{C}$ and $\text{Ti}_3\text{Au}_2\text{C}_2$ formed by solid state reaction of gold with Ti_2AlC and Ti_3AlC_2 . *ChemComm* **2017**, *53*, 9554-9557.
20. Lai, C.-C.; Fashandi, H.; Lu, J.; Palisaitis, J.; Persson, P. O.; Hultman, L.; Eklund, P.; Rosen, J., Phase formation of nanolaminated Mo_2AuC and $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ by a substitutional reaction within Au-capped Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ thin films. *Nanoscale* **2017**, *9*, 17681-17687.
21. Lai, C.-C.; Tao, Q.; Fashandi, H.; Wiedwald, U.; Salikhov, R.; Farle, M.; Petruhins, A.; Lu, J.; Hultman, L.; Eklund, P.; Rosen, J. Magnetic properties and structural

characterization of layered $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{AuC}$ synthesized by thermally induced substitutional reaction in $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$. *APL Mater.* **2018**, 6, 026104.

22. Schwarz, K., Band structure and chemical bonding in transition metal carbides and nitrides. *Crit. Rev. Solid State Mater. Sci.* **1987**, 13, 211-257.

23. Magnuson, M.; Mattesini, M.; Li, S.; Höglund, C.; Beckers, M.; Hultman, L.; Eriksson, O., Bonding mechanism in the nitrides Ti_2AlN and TiN : An experimental and theoretical investigation. *Phys. Rev. B* **2007**, 76, 195127.

24. Hug, G.; Fries, E., Full-potential electronic structure of Ti_2AlC and Ti_2AlN . *Phys. Rev. B* **2002**, 65, 113104.

25. Haddad, N.; Garcia-Caurel, E.; Hultman, L.; Barsoum, M. W.; Hug, G., Dielectric properties of Ti_2AlC and Ti_2AlN MAX phases: The conductivity anisotropy. *J. Appl. Phys* **2008**, 104, 023531.

26. Barsoum, M.; El-Raghy, T.; Ali, M., Processing and characterization of Ti_2AlC , Ti_2AlN , and $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$. *Metall. Mater. Trans. A* **2000**, 31, 1857-1865.

27. Eklund, P.; Beckers, M.; Jansson, U.; Höglberg, H.; Hultman, L., The $\text{M}_{n+1}\text{AX}_n$ phases: Materials science and thin-film processing. *Thin Solid Films* **2010**, 518, 1851-1878.

28. Fashandi, H.; Andersson, M.; Eriksson, J.; Lu, J.; Smedfors, K.; Zetterling, C.-M.; Spetz, A. L.; Eklund, P., Single-step synthesis process of Ti_3SiC_2 ohmic contacts on 4H-SiC by sputter-deposition of Ti. *Scr. Mater.* **2015**, 99, 53-56.

29. Kizaki, Y.; Mori, M.; Saito, M. In Development of Au-Al solid phase diffusion flip chip bonding, Proceedings of 1995 Japan International Electronic Manufacturing Technology Symposium, IEEE: 1995; pp 105-108.
30. Philofsky, E. In Purple plague revisited, 8th Reliability Physics Symposium, IEEE: 1970; pp 177-185.
31. Persson, K., Materials Data on Ti_2AlN (SG:194) by Materials Project. ; LBNL Materials Project; Lawrence Berkeley National Lab. (LBNL), Berkeley, CA (United States): 2016.
32. Predel, B., Al-Au (Aluminum-Gold). In *Ac-Au-Au-Zr*, Springer: 1991; pp 1-8.
33. Cullity, B. D., Elements of X-ray Diffraction. **2001**.
34. Musher, J. N.; Gordon, R. G., Low-temperature CVD TiN as a diffusion barrier between gold and silicon. *J. Electron. Mater.* **1991**, *20*, 1105-1107.
35. Mühlbacher, M.; Greczynski, G.; Sartory, B.; Mendez-Martin, F.; Schalk, N.; Lu, J.; Hultman, L.; Mitterer, C., TiN diffusion barrier failure by the formation of Cu_3Si investigated by electron microscopy and atom probe tomography. *J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom.* **2016**, *34*, 022202.

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Table of Contents graphic

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