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Low temperature thermal ALD TaN_x and TiN_x films from anhydrous N_2H_4

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ARTICLE INFO	A B S T R A C T				
Keywords: ALD Titanium nitride Tantalum nitride Organometallic XPS	Thermal ALD of TaN _x and TiN _x films was performed using hydrazine (N ₂ H ₄) as a reactive N-containing source. Ultralow temperature (100 °C and 300 °C) growth of TaN _x was observed using N ₂ H ₄ and tris(diethylamido)(<i>tert</i> - butylimido) tantalum (TBTDET); XPS showed nearly stoichiometric Ta ₃ N ₅ films were deposited with below 10% O and 5% C incorporation. Stoichiometric TiN _x films grown at 300 °C with tetrakis(dimethylamido) titanium (TDMAT) showed an RMS roughness below 2 nm consistent with good nucleation density. High conductivity nitride films were grown by a thermal low-temperature TiN _x ALD process using anhydrous N ₂ H ₄ and titanium tetrachloride (TiCl ₄) from 300 to 400 °C; uniform, nearly stoichiometric films of 0.44 nm RMS roughness were deposited. Compared to NH ₃ grown films, XPS confirmed N ₂ H ₄ grown films contained fewer O, C, and Cl im-				
	purifies consistent with lower resistivities being observed with N_0H_4 . The data is consistent with N_0H_4 serving as				

a reducing agent and a good proton donor to Ta and Ti ligands.

1. Introduction

Deposition of ultra-thin barrier layers on high aspect ratio features is a crucial processing component in microelectronic devices. As such, the need to deposit precise conformal barrier layers with thickness and stoichiometry control via an atomic layer deposition process is required. Two such barrier layers, titanium nitride (TiN) and tantalum nitride (TaN) have been extensively studied in devices because of their ideal thermal, mechanical, and electrical properties and ability to act as metal diffusion barriers [1–4]. In particular, TiN has been shown to act as an efficient diffusion barrier to WF₆ during W metal fill [3]. Similarly, tantalum nitride (TaN) has been utilized as a diffusion barrier to Cu on low-k insulators, such as SiO₂ or SiOCH, as Cu can readily diffuse into insulators lowering device reliability [5,6]. ALD TiN and TaN films have previously been performed using a wide range of precursors including halides (i.e. TiI₄, TiCl₄, TaCl₅, TaF₅) [1,7-9] and metal organics (i.e. TDMAT, TEMAT, TBTDET) [6,10-14], as well as nitrogen sources (thermal/plasma NH₃, N₂/H₂, etc). Metal halide precursors are typically preferred over organometallic grown films to lower impurities when there is no concern about metal corrosion, such as in capping HfO₂ [15] or for TiN/HfO₂ gate stacks [16]. In comparison, organometallic-grown films usually contain higher levels of residual carbon

and oxygen contamination, which has been correlated with an increase in film resistivity [13,14]. Commercial processing on 200 and 300 mm wafers showed that $TiCl_4 + NH_3$ at 400 °C achieved low resistivities for films approximately > 20 nm [17], but plasma enhanced-ALD TiN was needed achieve optimal growth rates with lower contamination at temperatures near 350 °C; however, the film and underlying substrate can suffer from plasma-induced damage [1,18].

For the results presented in this work, low-temperature thermal deposition of TaN and TiN films using sequential exposures of anhydrous N_2H_4 [19] and either TBTDET, TDMAT, or TiCl₄ were performed. Insulating SiO₂/Si substrates were utilized in order to perform electrical characterization of deposited films. Since anhydrous N_2H_4 was used as the reactive nitrogen source, the barrier for surface reactions to occur with each precursor can be reduced compared to using thermal NH₃; the dissociation of N_2H_4 through the breaking of a N–N bond is more energetically favorable than having to dissociate a more tightly bound N–H bond in NH₃. The N–N single bond in N_2H_4 has an energy of ~ 3 eV, while the N–H single bond in NH₃ has an energy of ~ 4.5 eV [20]. Moreover, the purity of the N_2H_4 allows for deposition of films without uptake of oxygen or carbon contamination, which has previously been demonstrated with SiN_x [21] and BN [22] films. A novel metal halide TiN_x ALD process was developed with TiCl₄ and N_2H_4 that

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produced resistivities of 593 µohm-cm and 359 µohm-cm at 300 °C and 400 °C, respectively that could readily be incorporated into MOS gate stack architectures. Note, this is the first time ALD titanium nitride has been reported in the literature with TiCl₄ and N₂H₄.

2. Experimental methodology

The substrates used in this study consisted of 300 nm of thermal SiO₂ grown on Si(001) (University Wafer). Samples underwent an ex situ degrease involving quick rinses in acetone, methanol, and water before being loaded into the vacuum chamber. Once loaded into the UHV chamber, the samples were heated to 350 °C for 30 min to remove any physisorbed surface contamination. Precursor exposures were performed in a deposition chamber, which has been described in detail elsewhere [22]. The deposition chamber and dosing lines were pumped with a turbomolecular pump, but the actual deposition was performed through only a backing pump with a base pressure of $\sim 1 \times 10^{-2}$ Torr. The chamber was heated ~ 100 °C, and dosing lines were kept ~10-20 $^{\circ}$ C warmer to ensure precursors would not condense on the chamber walls. In addition, the N2H4 vessel was pressurized to \sim 750 torr with ultrahigh purity N₂ that was passed through a purifier to act as a push gas for the N2H4·NH3 from Praxair with a purity of 99.9% was used for TiNx experiments undiluted. Precursor exposures are presented in MegaLangmuirs (MegaLs where 1 MegaL = 1 Torr for 1 sec), and were calculated from exposure time and pressure of the precursor; however, it should be noted that the values presented for exposures of N₂H₄ do not account for the dilution with N₂. As an estimation, by using the vapor pressure of N₂H₄ at room temperature, the amount of N_2H_4 was likely ~ 1–2% of the total exposure. Before moving samples into the deposition chamber, samples were preheated in the UHV chamber. In both chambers, samples were radiatively heated by a pyrolytic boron nitride heater. After exposure to anhydrous N₂H₄ (Rasirc) and either TiCl₄ (Strem Chemicals), TDMAT (Sigma-Aldrich), or TBTDET (Sigma-Aldrich) samples were transferred back to the UHV chamber where in situ x-ray photoelectron spectroscopy (XPS) was performed without breaking vacuum. A monochromatic XPS system (Al $k\alpha h\nu = 1486.7 \text{ eV}$) was used to collect surface-sensitive spectra at an angle of 60° with respect to the surface normal. Additionally, an electron pass energy of 50 eV and a line width of 0.1 eV were used. XPS spectra analysis was conducted with CASA XPS v.2.3 utilizing Shirley background subtractions. Schofield photoionization cross sectional relative sensitivity factors were used to correct raw peak areas before normalization. In addition to XPS, surface topography was characterized with atomic force microscopy (AFM). Lastly, the resistance of airexposed thin films was measured using a modified four-point probe measurement, in which 30 nm thick Ni dots with $150\,\mu\text{m}$ diameters and $250 \,\mu\text{m}$ spacing were deposited on top of ALD TiN_x and TaN_x films. Resistivities were approximated by estimating the thickness of deposited films from cross-sectional scanning electron microscopy (SEM) images. Note the resistivities were measured after air exposure so the actual TiNx thicknesses are probably less than those measured by SEM since the top few nanometers may have been oxidized and converted to high resistivity TiO_xN_y [23].

3. TaN_x from TBTDET

Anhydrous N_2H_4 chemistry was applied to ALD at very low temperatures with an organometallic Ta precursor (TBTDET); saturation data documenting the ALD deposition at 150 °C is shown in Fig. 1 (the related raw XPS spectra for XPS histogram data are shown in the supplement). Higher sample temperature saturation was not tested because the uniformly high valance of the Ta in the film showed the N_2H_4 did not have the ability to reduce the Ta in the TDTBET; instead the data was consistent with the need for a lower valent Ta precursor for reaction with N_2H_4 to form conductive TaN. As shown in Fig. 2, AFM imaging indicated a pinhole-free surface with a low RMS surface



Fig. 1. XPS Saturation Study of TBTDET and N₂H₄ on Degreased SiO₂/Si at 150 °C. Initial 1x (3 MegaL) TBTDET dose deposited 6.4% Ta on UHV annealed SiO₂/Si. Additional 2x (6 MegaL) TBTDET saturated Ta at 8.0%, while depositing 1.0% N. Similarly, a 1x (15 MegaL) and a 2x (30 MegaL) dose of N₂H₄ were performed, which saturated the N at 2.6%. Self-limiting exposures were consistent with ALD. The TBTDET bottle was heated to ~80 °C and utilized an N₂ carrier gas to help deliver TBTDET to the sample.



Fig. 2. Ex Situ AFM Imaging. 15 cycles of TaN_x at 150 °C from TBTDET + N_2H_4 . The deposited film showed a very low RMS surface roughness of 0.25 nm and no evidence of pinholes.

roughness of 0.25 nm from 15 cyclic exposures of TBTDET and N2H4 at 150 °C. Fig. 3 shows the XPS of TaN_x films at temperatures between 100 °C and 300 °C. In Fig. 3(a), XPS normalization shows that the films contain nearly 40% C at 100 °C and almost 30% at 300 °C; however, the amount of O is undetectable at 100 °C and only ~4% at higher temperature. Fig. 3(b) shows the raw Ta 4d peak that confirmed the nucleation with TBTDET (Si-O-Ta formation) based on the Ta 4d peak position of ~231 eV [24,25]. After ALD cycles of TBTDET + N2H4, there was an $\sim 2 \,\text{eV}$ chemical shift toward lower binding energy consistent with formation of Ta-N bonds in the film. It is noted that the ratio of Ta to N in the deposited films becomes more Ta rich at increasing deposition temperatures. This effect is observed more clearly when looking at the Ta $4p_{3/2}$ / N 1 s region; at higher temperature the N peak shifts to lower BE and becomes more narrow while the Ta component increases in intensity (Fig. 3(d)). In Fig. 3(c), a dose of atomic H at 250 °C was performed on the 150 °C grown film; the C is significantly reduced to $\sim 1.5\%$. This result was consistent with the C simply accumulating on the top of the film during deposition. The changing Ta/N ratio before and after the 250 °C atomic H exposure in the normalized XPS is most consistent with annealing in the presence of atomic H inducing desorption of a C_xN_yH_z species from the surface (as seen in Figs. 3 and 4).

Fig. 4 shows the XPS Ta $4p_{3/2}$ / N 1 s region for a series of experiments in which the clean surface underwent a total of 100 ALD cycles at a deposition temperature of 100 °C followed by UHV anneals up to 250 °C. During the ALD dosing, there was a broad N 1 s component located at a BE of ~ 399 eV along with a very weak Ta $4p_{3/2}$ signal at ~ 404 eV. Upon annealing, the Ta $4p_{3/2}$ component becomes stronger,



Fig. 3. TaN_x deposition from TBTDET + N₂H₄. (a) XPS of 100 cycles of TBTDET and N₂H₄ at 100 °C, 150 °C, and 300 °C. (b) The Ta 4d XPS peaks after 6 pulses of TBTDET and after 15 TaN_x cycles. The initial 6 pulses confirmed interfacial Si–O–Ta bond formation, while after 15 cycles an ~2 eV shift is seen consistent with formation of Ta–N bonds. (c) 15 min of atomic H were enough to remove the carbon that was accumulating on the surface during deposition. (d) Ta $4p_{3/2} / N$ 1 s region showing the N 1 s component shifting and narrowing as a function of ALD temperature.



Fig. 4. XPS of TaN_x Cycles at 100 °C and Post Deposition Anneal (PDA). XPS was performed after subsequent cycles of TaN_x ALD at 100 °C. After 100 total cycles, a 150 °C, 200 °C, and 250 °C anneal were performed each for 30 min. Note the shift in the N 1 s peak, as well as additional intensity in the Ta $4p_{3/2}$ component upon annealing.

and the N 1 s peak narrows and shifts toward lower BE. This observed change in the N 1 s peak is consistent with the loss of surface CH_xN_y surface species and consistent with the formation of partially crystalline Ta_3N_5 as previously reported in the literature [26]. When trying to determine the precise oxidation state of the Ta to ascertain if the film is more like conductive TaN [27] or insulating Ta_3N_5 [7], it is not sufficient to just analyze the Ta 4p region; further evidence of Ta being in an oxidation state higher than + 3 can be seen when looking at the peak position of the Ta 4f (see supplement). From the literature, this corresponds much closer to an average oxidation state of at least Ta⁺⁴ [26]. Lastly, resistance measurements were performed on several TaN_x samples; measurements indicated highly resistive films consistent with higher oxidation state Ta TaN_x films. Previous work studying TaN_x deposition with these precursors similarly resulted in higher than expected resistivity values due to an inability to deposit Ta rich films [10].

4. TiN_x ALD

4.1. TDMAT

In addition to growing films with TiCl₄, TiN_x deposition with N₂H₄ and TDMAT was performed. TDMAT grown films are useful for backend processing where using metal-halide precursors, such as TiCl₄ are prohibited due to issues of metal corrosion. Fig. 5(a) depicts the XPS chemical composition of 100 cycles TDMAT grown films at 300 °C utilizing a 5s pump after TDMAT exposure and before the following N₂H₄ half cycle. This short pump out time of TDMAT allowed for lower oxygen at ~5% compared to longer pump times where background oxygen and water can incorporate into the film. Fig. 5(b) shows the AFM image and corresponding line trace of the deposited film at 300 °C. The RMS surface roughness was 1.73 nm, about 4x higher than the TiCl₄ process (see below), which is likely due to the significant C accumulation on the surface. Fig. 5(c) plots the Ti 2p raw peaks as a function of the TDMAT pump time. It can be seen that for longer pump cycles, the Ti 2p peak position is shifted toward higher BE. This is consistent with background oxygen and/or water reacting with the film before the incoming N₂H₄ completely passivates the surface. Resistance measurements were performed on several deposited TDMAT grown films; the 5 s pump cycle sample had the lowest resistance, \sim 3,840 O (Fig. 5(d)). In SEM, the sample showed a thickness of nearly 50 nm, which places the estimate for resistivity at $\sim 87,000 \mu$ ohm-cm.

4.2. TiCl₄

Fig. 6 shows the XPS results from saturation dosing that was performed on SiO₂/Si at 300 °C. After undergoing a UHV anneal at 350 °C, the first 1x exposure of 10 MegaL TiCl₄ was dosed and reacted on the surface, evidenced by the 0.5% Ti and 2.2% Cl observed in XPS. Subsequently, an additional 2x exposure of 20 MegaL TiCl₄ saturated the Ti at 0.6% and Cl at 2.4%. In a similar manner, N₂H₄ saturation dosing



Fig. 5. TDMAT Grown TiN_x Films: (a) XPS and (b) AFM of 100 cycles TiN_x at 300 °C grown with N₂H₄. (c) The Ti 2p peak positions as a function of TDMAT pump time before N₂H₄ exposure. The position is compared to TiCl₄ processing. (d) Resistance measurement of TDMAT grown films with a 5 s pump.

was performed using subsequent exposures to a 1x, 2x, and 3x dose where a 1x exposure equals 15 MegaL of N_2H_4 diluted in N_2 . After the final 3x dose, the Cl dropped from 2.4% to 1.4%, and the N saturated at 0.8%. This evidence of saturating half-cycle dosing is consistent with a low-temperature thermal ALD procedure utilizing 10 MegaL TiCl₄ + 45 MegaL N_2H_4 . It should be noted that these large saturation exposures determined from the growth initiation may differ from the amounts needed for steady state deposition. However, during steady state dosing, the density of reactive sites is likely higher than the starting SiO₂ surface providing sufficient confidence that saturated dosing was performed throughout all cycles. This was confirmed by XPS measurements showing that substrate peaks continuously diminished with the number of cycles in a manner consistent with a constant growth rate per cycle (see supplement).

Once the required pulse size of each half-cycle was determined from the saturation study, thicker films of TiN_x were grown using the saturated recipe of 10 MegaL TiCl₄ and 45 MegaL N₂H₄. Fig. 7(a) shows the corrected and normalized XPS of 40 cycles TiN_x at 300 °C. The composition of the 40 cycles film indicated that there was ~ 20% residual Cl that could be left in the film or on top of the film as a Cl accumulation layer; however, the chemical shift data for Ti in Fig. 7(b) showed only a small Ti-Cl component in the bulk of the film, consistent with the residual Cl mainly being a surface layer. The level of attenuation of the Si 2p substrate is consistent with 40 cycles being ~ 5 nm thick.

Fig. 7(b) shows the raw Ti $2p_{3/2}$ and $2p_{1/2}$ spin orbit peaks. A lower binding energy (BE) component located at ~455 eV was consistent with Ti–N bonds, as previously reported in the literature [28,29]; it is also known that stoichiometric TiO₂ has a BE near 458–459 eV [30,31]. Additionally, since, the deposited film also contains Cl residue, Cl bonds cannot be neglected, and Ti–Cl bonds are known to have a Ti $2p_{3/2}$ BE of ~458.5 eV as well [32,33]. Therefore, the component that is located at ~456.5 eV is consistent with a higher N content TiN_x (likely Ti₃N₄) or a substoichiometric TiO_x [34]. However, as shown in Table 1, the high conductivity of the films is consistent with only trace TiO_x in the bulk of the film. It should be noted that precise fitting of the Ti 2p peak was difficult due to the numerous Ti chemical states, as well as the wide range of XPS BE values reported in the literature for TiN, TiN_x, and TiO_xN_y films [31]. Therefore, for definitive documentation of deposition of TiN, resistivity measurements are required.

In order to perform four-point probe measurements to check the

Fig. 6. XPS Saturation Study of TiCl₄ and N₂H₄ on Clean SiO₂ at 300 °C. Initial 1x TiCl₄ dose deposited 2.2% Cl and 0.5% Ti on UHV annealed SiO₂/Si. Additional 2x TiCl₄ saturated Cl at 2.4% and Ti at 0.6%. Similarly, a 1x, 2x, and 3x dose of N₂H₄ were performed, which saturated the Cl at 1.4% and N at 0.8%. Self-limiting exposures were consistent with ALD.





Fig. 7. Growth of TiN_x Film at 300 °C. (a) Normalized and corrected XPS of 40 cycles TiN_x at 300 °C on a UHV annealed surface. The 300 °C film contains significant Cl residue. (b) Raw XPS outlining the various components that are present in the Ti 2p spectra.

 Table 1

 Summary of TiNx Films Grown with NH3 and N2H4.

Nitrogen Precursor	Temperature (°C)	Residual Chlorine (%)	Number of Cycles	SEM Thickness	Growth Rate (nm/cycle)	Resistivity (µohm-cm)
$\begin{array}{c} \mathrm{NH}_3\\ \mathrm{NH}_3\\ \mathrm{N}_2\mathrm{H}_4\\ \mathrm{N}_2\mathrm{H}_4 \end{array}$	300	16.0	80	13	0.16	2,885
	400	12.1	40	18	0.45	554
	300	18.1	80	17	0.21	593
	400	8.7	40	11	0.28	359



Fig. 8. Effect of Air Exposure. (a) 40 cycles TiN_x at 300 °C followed by 1 min, 5 min, and 60 min of air exposure. (b) Ti 2p raw XPS peaks showed an ~1.5 eV BE shift after just 1 min of air exposure. After 1 h, the TiN component located at 455 eV was significantly reduced.

resistivity of deposited films, TiNx films must be exposed to ambient air conditions for ~ 1 h. To quantify the effect of the air exposure, XPS was performed after 1 min, 5 min and 60 min of ambient exposure. Fig. 8 displays the Ti 2p peak as a function of air exposure times. Along with increasing the amount of surface oxygen and carbon, the oxidation state of the Ti underwent a significant shift. Before ambient exposure, the maximum of the Ti 2p 3/2 peak appeared at 456 eV with a strong TiN component at 455 eV; however, even after just 1 min of air exposure, O attacked the TiN_x film, evidenced by observing an ~ 1.5 eV BE shift of the Ti 2p 3/2 peak. After 60 min of air exposure, the maximum peak position shifted by about 2 eV, as well as a significant decrease in the TiN component at \sim 455 eV. Additionally, this oxidation could increase the film thickness that was determined with SEM (see supplement). Both of these effects would be expected to lead to increases in the reported resisitivites in this manuscript, as compared to hypothetical resistivity measurements in situ.

To characterize the surface topography, AFM was performed on the 40 cycles of ALD TiN_x film. Fig. 9(a) depicts the bare *ex situ* cleaned surface and (b) after deposition. AFM imaging along with corresponding line traces show the pinhole-free AFM image of 40 cycles of TiN_x at 300 °C compared with the bare SiO₂ surface. Additionally, the deposition was uniform as evidenced by maintaining a low RMS surface roughness of 0.44 nm.

To study the efficacy of N₂H₄ as a TiN precursor, thermal NH₃ was used for comparison. Fig. 10 shows the comparison of TiN_x films grown at 400 °C with (a) NH₃ and (b) N₂H₄; there was approximately 2x more O and C and 50% more Cl in 400 °C NH₃ grown films. The source of this increased O incorporation when using NH₃ could arise from side reactions with H₂O/O₂ that can occur from incomplete reaction with NH₃. The higher reactivity of N₂H₄ may rapidly cover the surface with NH_x ligands thereby reducing contamination from background H_2O/O_2 . Fig. 10(c) and (d) show the corresponding resistances measured for NH_3 and N₂H₄ grown films, respectively. It should be noted that the ratio of Ti/N for NH₃ grown films is > 1, while for N_2H_4 grown films it is < 1; however, the amount of O, C, and Cl impurity incorporation prevents the NH₃ grown film from becoming more N-rich, and correspondingly, more conductive. Table 1 summarizes the results of TiN_x films utilizing TiCl₄ and either N₂H₄ or NH₃. N₂H₄ films showed lower resistivities, attributed to lower contamination and likely better nucleation density. The best result of 400 °C N₂H₄ showed the lowest residual Cl at 8.7%, which correlated with being the lowest resistivity film estimated at 359 µohm-cm. From the air exposure XPS study, approximately the top 2 nm of the TiN_x films were converted to TiO_xN_y / surface contamination; thus the thickness of TiN_x may be as low as 9 nm so the intrinsic resistivity could equate to as low as 294 µohm-cm for the 400 °C N₂H₄ film.



Fig. 9. Ex Situ AFM Imaging. (a) Bare SiO₂ and (b) 40 cycles TiCl₄ + N₂H₄ at 300 °C. The low RMS surface roughness was indicative of conformal TiN_x growth.



Fig. 10. NH_3 vs. N_2H_4 Grown TiN_x Films: 40 cycles TiN_x at 400 °C grown with (a) NH_3 and (b) N_2H_4 . The amount of O and C was ~2x larger with the Cl being 50% higher in NH_3 grown films. Resistance measurements for (c) NH_3 and (d) N_2H_4 grown TiN_x films.

5. Discussion and conclusion

The anhydrous N_2H_4 chemistry was used with organometallic precursors, TBTDET and TDMAT. For both precursors, thermal processing could not remove all the impurities from the film. For TBTDET, the films deposited were N-rich at low temperature, but became more stoichiometric at higher temperature. Even though an atomic H exposure was able to reduce the level of C impurity, the TaN_x films

displayed insulating behavior. For TDMAT grown films, the oxidation state of the Ti (from the Ti $2p_{3/2}$ component) was more oxidized than the Ti from the TiCl₄ process. In the literature, it is well known that atomic H from plasma is required to help reduce the metal, typically through the formation of a more conductive carbide phase [35,36]. In order to achieve more conducting films with organometallic precursors from non-plasma processing, lower valence Ti and Ta precursors need to be developed and tested. It is expected that lower valence precursors reacted with N₂H₄ would produce more conductive films.

Thermal low-temperature TiN_x ALD cycles using anhydrous N₂H₄ and TiCl₄ were performed at 300–400 °C, and subsequently, conformal, nearly stoichiometric films were deposited as seen in XPS and AFM. Compared to NH₃ grown films, N₂H₄ grown films at both 300 °C or 400 °C showed lower resistivities with fewer impurities. Reported resistivities are likely higher due to significant oxidation of the ultra-thin films, but are still near the best values reported in the literature values for ALD TiN_x films [14,37]. In particular, the authors believe the 300 °C thermal N₂H₄ grown TiN_x film with a resistivity of 593 µohm-cm to be the lowest resistivity film reported for this temperature and thickness.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://10.1016/j.apsusc.2018.07.153.

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