ALD Fundamentals
Room On Demand - Session AF9

Growth and Characterization: Characterization of ALD Films

AF9-1 Smoothing Surface Roughness Using Al_2O_3 Atomic Layer Deposition, ***Tyler Myers***, University of Colorado Boulder; *J. Throckmorton, R. Borrelli, M. O'Sullivan, T. Hatwar,* L3Harris; *S. George,* University of Colorado Boulder

Surface roughness can affect many areas such as optical scattering, friction, adhesion and semiconductor device performance. There are various methods for smoothing surfaces including chemical mechanical polishing (CMP) and chemical etching. However, these methods are abrasive and corrosive and can be detrimental. Atomic layer deposition (ALD) deposits conformal films that can "pinch off" surface roughness by filling in the gaps between surface asperities. In this study, Al_2O_3 ALD was used to smooth rough silicon wafers and improve the optical reflectivity of Ag mirrors deposited on the silicon wafers.

Al_2O_3 ALD was performed on rough, pre-CMP silicon wafers. Al_2O_3 was deposited at 200°C using trimethylaluminum (TMA) and water (H_2O) as the reactants. Al_2O_3 ALD films of various thicknesses were grown on the silicon wafers using up to 4000 Al_2O_3 ALD cycles. The RMS roughness was measured using atomic force microscopy (AFM). AFM showed that the original rough, pre-CMP silicon wafers had an RMS roughness of 3.5 nm. AFM line scans measured an average lateral spacing between the surface asperities of 400 nm (Figure 1a). After 3000 Al_2O_3 ALD cycles, the RMS roughness of the wafers was reduced to 1.5 nm and the average lateral spacing between the surface asperities increased to 700 nm (Figure 1b).

The RMS roughness decreased progressively with number of Al_2O_3 ALD cycles (Figure 2). The minimum surface roughness of 1.5 nm was reached after 3000 cycles. Additional Al_2O_3 ALD cycles then produced little change in the RMS roughness. The smoothing is believed to limit when the lateral distance between the surface asperities is much larger than the Al_2O_3 ALD film thickness. Power spectral density (PSD) analysis revealed that the ALD smoothing was most effective for surface topographical features with lateral spacings in the range of 10s to 100s of nanometers. The PSD analysis showed that most of the smoothing occurs during the first 1000 Al_2O_3 ALD cycles. Reflectivity studies of Ag mirrors deposited on the silicon wafers demonstrated that Al_2O_3 ALD smoothing improves the optical performance of reflective mirrors.

AF9-2 Effect of Oxidant on Film Properties of HfO_2 grown via Atomic Layer Deposition using Newly Synthesized Cp-based Hf Precursors, ***Seonyeong Park***, *H. Yoon, Y. Lee, S. Lee, H. Lee, S. Chung, H. Kim,* Yonsei University, Korea

With the scaling down of semiconductor devices, SiO_2 was replaced by high-k materials due to increased leakage current. Among the various high-k materials, HfO_2 has been widely used owing to its high dielectric constant (~25) and suitable band offset with Si (~1.4 eV).[1] For ultrathin high quality HfO_2, atomic layer deposition (ALD) has been used. Through ALD technology, atomic layer controlled HfO_2 film with high conformality and high uniformity can be obtained. For HfO_2 ALD technology, various precursors such as halides, alkoxides, alkylamides, and β-diketonates have been applied. Using halide precursor, HfO_2 films do not have C impurities. However, corrosive byproducts such as HCl can degrade the film quality.[2] Furthermore, halide precursors have low volatility which means that high temperature is needed to get HfO_2 films.[2] Alkoxides have strong metal-O bonds, so that they require high temperature for deposition process. In addition, β-diketonates are not proper precursors for ALD, because they have bulky ligands which leads to steric hindrance and have low volatility.[1] β-hydride elimination causes hydrolytic decomposition of β-diketonates, which leads to the non-saturated growth characteristics. Since alkylamides have weak metal-N bonds, they are highly reactive at low temperature. Although alkylamides are widely used for ALD process, they are easily decomposed at high temperature.[1] Therefore, there can be a lot of impurities on thin films deposited with ALD. By employing cyclopentadienyl (Cp) ligand as functional ligand group of heteroleptic precursor, thermal stability and volatility of alkylamide precursors are improved.[1] Research has been conducted to increase thermal stability of precursors by increasing the number of Cp ligands. However, even that has now reached its thermal stability limit, requiring a precursor available at higher temperatures. We newly synthesized the Hf precursor which is stable at higher temperature. We investigated the effect of oxidants on film properties of HfO_2 using newly synthesized Cp-based alkylamide Hf precursor.

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AF9-3 Advanced Wafer Scale Uniformity Characterization Method for Conformal 3D Thin Films, ***Mikko Utriainen***, *P. Hyttinen, F. Gao,* Chipmetrics Ltd, Finland; *A. Bider, K. Saastamoinen, H. Rekola,* University of Eastern Finland, Institute of Photonics, Finland; *R. Puurunen,* Aalto University, School of Chemical Engineering, Finland; *O. Ylivaara,* VTT Technical Research Centre of Finland

Atomic layer deposition (ALD) enables uniform thin film coating over large substrate areas. Besides thickness uniformity, today's memory and MEMS applications with three-dimensional structures require good conformality over high aspect ratio (HAR) structures. The state-of-art method to define wafer scale uniformity is film thickness mapping. Easy wafer level conformality characterization from 3D HAR structured wafers is hardly accessible due to challenging high-resolution cross-sectional measurements. PillarHall® Lateral High Aspect Ratio (LHAR) silicon test chip has already proven its value in conformality metrology and even in the characterization of the thin film properties inside deep cavity walls [1,2,3] without cross-sectioning. The purpose here is to study further the consistency, sensitivity and accuracy of the wafer level uniformity and conformality analysis using PillarHall® LHAR4 test chip (Chipmetrics Ltd) on 150 and 200 mm silicon carrier wafers. Chips were placed evenly over the studied substrate area. An analysis was made using simple optical measurement tools such as optical modelling software, optical microscopy with image analysis, and reference reflectometry measurements. Experimental work consisted of several thermal ALD processes (Al_2O_3, SiO_2, TiO_2 and TiN). ALD reactors were Picosun R-150 and Beneq TFS-200. Optical microscope image analysis was used to assess conformality analysis accuracy using ALD Al_2O_3 on LHAR samples from various positions of the wafer area. The results show good accuracy and are in line with optical modelling outcome and in agreement with reflectometry data. Optical modelling also enables predictions of the method compatibility and limitations with various other thin-film materials. When comparing the ALD Al_2O_3 data to the simultaneous flat substrate thickness mapping, it is shown that PillarHall® method is a sensitive measure for wafer-level uniformity and conformality mapping. The presented method is widely compatible to ALD and related 3D thin film processes and can accelerate their industrial applications.

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AF9-4 Thermal Atomic Layer Deposition of Silicon Nitride Using Anhydrous Hydrazine and Ammonia, ***Dan N. Le***, *S. Hwang, J. Mohan, J. Kim, Y. Jung,* University of Texas at Dallas; *D. Alvarez, J. Spiegelman,* RASIRC; *J. Kim,* University of Texas at Dallas

In this study, a thermal atomic layer deposition (t-ALD) for silicon nitride (SiN_x) is established at the temperature window of 320–600°C. Hexachlorodisilane (HCDS) and high purity anhydrous hydrazine (N_2H_4) are utilized as the precursors for silicon and nitrogen, respectively. The characteristics of deposited films are analyzed by the growth per cycle (GPC), refractive index (R.I.), wet-etch rate (WER), and chemical composition. The electrical properties of SiN_x deposited using N_2H_4 are also studied using "metal-insulator-metal (MIS)" structure. -*in-situ* FTIR technique is employed to examine the bonding information.

At 480°C, the GPC of silicon nitride gradually increases with an increase in the N_2H_4 pulse time (0.2, 0.5, 1.0, and 2.5 s). SiN_x exhibits a growth rate of 0.031 nm/cycle with 0.5-second N_2H_4 exposure time at the working pressure of 150 mTorr. At the same deposition temperature (480°C) and hydrazine exposure time (0.5 s), the GPC at 500 mTorr is 0.048 nm/cycle.

Within the temperature range of 390–520°C, the growth per cycle is nearly constant, with the approximate value of 0.049 nm/cycle. Furthermore, silicon nitride thin films are also grown using ammonia (NH_3) as references. Under identical deposition conditions (exposure time, temperature, and working pressure), ammonia delivers a lower growth rate (~0.019 nm/cycle) than hydrazine. As the deposition temperature increases, the refractive index of SiN_x grown with hydrazine increases (as high as 1.99), while the WER significantly decreases with the etch rate as low as 0.37 nm/min in 200:1 HF diluted solution. At 480°C, silicon nitride grown using hydrazine and ammonia has a density of 2.73 and 2.69 g/cm^3, respectively. The R.I. and WER values are 1.86 and 2.24 nm/min for hydrazine, while 1.96 and 7.48 nm/min for NH_3. The chemical composition of SiN_x grown with N_2H_4 is 54±1.0 [Si] at.%, 44±1.0 [N] at.%, 2±1.0 [O] at.%, and <1.0 at.% [Cl] (under the detection limit). The deposited silicon nitride has a leakage current density as low as approximately 12.0±0.2 nA/cm^2 and a break down field as high as 12.8±0.2 MV/cm.

Ovanesyan *et al.* and Meng et al. suggested that HCDS reacts with $–NH_2$ groups on the surface and leaves –NH– groups as the primary form of hydrogen bonds in SiN_x.[1,2] *in-situ* FTIR is used to investigate the different surface reaction pathways between N_2H_3 and NH_3. Experimental details and results will be presented.

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AF9-5 Importance of XPS Investigations of ALD Grown 2D Materials*,* ***Jhonatan Rodriguez Pereira,*** University of Pardubice, Czechia*; R. Zazpe, H. Sopha,* University of Pardubice; Central European Institute of Technology, Brno University of Technology, Czechia*; F. Bures,* University of Pardubice, Czechia*; J. Macak,* University of Pardubice; Central European Institute of Technology, Brno University of Technology, Czechia

The success of graphene opened a door for a new class of semiconducting 2D transition metal chalcogenide materials (TMDs) displaying unique properties [1]. ALD MoS_2, as TMDs benchmark, has been widely studied for several applications. In parallel, 2D selenide and telluride analogues, i.e. $MoSe_2$ and $MoTe_2$, have also attracted important interest due to intriguing properties, such as a higher electrical conductivity than that of MoS_2 among others [2, 3].

Recently, we have demonstrated the ALD synthesis of both 2D $MoSe_2$ [4-7] and 2D $MoTe_2$ [8] (using an in-house synthesized precursors), as well as their outstanding performances in different applications. XPS turned a key tool to provide detailed chemical composition analysis of as-deposited 2D Mo TMDs family on different nature substrates. Besides, the post-performance XPS characterization was appealing since the applications of the aforementioned 2D materials involved chemical and/or electronic processes on the surface and it enabled to identify potential chemical composition changes and physicochemical photo-electro stability of the 2D TMDs. This presentation will thus focus on the XPS as key tool for assessment of chemical composition of both as-deposited and post-performance 2D Mo TMDs family, recent experimental results as well as the description of some inherent drawbacks that XPS must face during the analysis of the 2D materials.

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AF9-6 Microstructure and Mechanical Properties of Atomic Layer Deposited Alumina Doped Zirconia*,* ***Helle-Mai Piirsoo,*** University of Tartu, Estonia

ZrO_2 metastable polymorphs possess higher hardness and elastic modulus compared to the monoclinic phase that could increase the mechanical endurance of the material [1-2]. Metastable phases of ZrO_2 could be obtained at ambient conditions with a low film thickness or by doping with foreign metal oxides [3-4]. Atomic layer deposited ZrO_2 thin films with high mechanical resilience could be applied as protective coatings.

In the present study, Al_2O_3-doped ZrO_2 films were atomic layer deposited on TiN/Si substrate at 300°C with $ZrCl_4$, $Al(CH_3)_3$ and H_2O. One $Al(CH_3)_3$ + H_2O cycle was performed between every 2, 4, 9, 14 and 19 consecutive cycles of $ZrCl_4$ + H_2O. The thickness of the films neared 100 nm.

Grazing incidence X-ray diffraction revealed that the film grown using ZrO_2: Al_2O_3 cycle ratio of 19:1 was crystallized in its tetragonal polymorph (Fig. 1). Increasing the Al_2O_3 content with cycle ratios of 14:1 and 9:1 stabilized the cubic polymorph. The films with higher Al_2O_3 contents remained amorphous and the reference ZrO_2 films was monoclinic. All the crystalline films possessed a preferential grain orientation to different extent beneath the surface and in the vicinity of the substrate.

Nanoindentation was used to determine the hardness and elastic modulus averaged over 30 indents in each film (Fig. 2). The most rigid films with hardness up to 15 GPa and elastic modulus above 167 GPa were obtained with cubic ZrO_2 stabilized with Al_2O_3. In general, the hardness and elastic modulus increased in the vicinity of the substrate even though the substrate possessed lower values of hardness (12 GPa) and elastic modulus (147 GPa). The texture in thin films had an effect on the mechanical properties.

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AF9-7 Friction and Wear Properties of Low-Temperature Metal Oxides*,* ***Oili Ylivaara****, L. Kilpi,* VTT Technical Research Centre of Finland*; R. Ritasalo,* Picosun Oy, Finland*; H. Ronkainen,* VTT Technical Research Centre of Finland

In microelectromechanical system (MEMS) devices, thin film made by atomic layer deposition (ALD) can be used as a functional material or as a protective coating due to its ability to coat high-topology surfaces with good conformality. In MEMS devices, there are moving parts involved and during its lifetime, device might be exposed to internal friction causing wear, and long-term reliability issues. Here, we studied low-temperature thin films made by ALD in a system where a silicon counterpart is sliding against ALD coating. Thin films were grown in a temperature range from 85 to 200 °C with a target thickness of 100 nm. Studied materials were Al_2O_3, TiO_2, Ta_2O_5, SiO_2, and some of their nanolaminates. Friction and wear properties of ALD coatings were evaluated with reciprocating sliding test using Anton Paar Tritec Pin-On-Disc tribometer. The load and sliding speed were kept constant during the testing, at 0.3 N and 0.01 m/s, respectively. Sliding distance was up to 20 meters using 10 mm back and forth movement. For each material, friction coefficient was measured during the testing, and after the testing wear surfaces on both the ALD coated silicon sample and silicon pin were analysed, and wear rate was calculated. On most coatings, friction coefficients were on the same level as with reference silicon. In case of the Al_2O_3 and TiO_2 visible tribolayer was formed in the wear surface. In the case of Ta_2O_5, besides tribolayer formation, coating was worn during the testing revealing silicon substrate. For SiO_2 both coating was worn and tribolayer was formed on the surface. Friction and wear results presented here give interesting options for low-temperature protection of the wear surfaces.

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AF9-8 Cryo-ePDF to Measure the Atomic Structure of Amorphous ALD Interfaces, ***Matthias Young***, *N. Paranamana, X. He, T. White,* University of Missouri-Columbia

Atomic layer deposition (ALD) provides uniform and conformal thin films that are of interest for a range of applications. To better understand the properties of amorphous ALD films and ALD-modified interfaces, we need improved understanding of their local atomic structure. Previous work demonstrated measurement of how the local atomic structure of ALD-grown aluminum oxide (AlO_x) evolves in operando during growth by employing synchrotron high energy X-ray diffraction (HE-XRD). In this work, we report on efforts to employ electron diffraction pair distribution function (ePDF) measurements using more broadly available transmission electron microscope (TEM) instrumentation to study the atomic structure of amorphous ALD-AlO_x and ALD-modified interfaces. We observe electron beam damage in ALD-coated samples during ePDF at ambient temperature and successfully mitigate this beam damage using ePDF at cryogenic temperatures (cryo-ePDF). We examine both wide-area electron diffraction over a ~200 nm spot size, as well as local diffraction over a <2 nm spot size using cryo-ePDF. The smaller spot size (achieved using convergent electron diffraction with a small convergence angle) allows for local electron diffraction, for example at multiple positions along the cross-section of a 10 nm thick ALD film, and enables characterization of the interfacial atomic structure of the ALD film relative to the bulk structure. We employ Reverse Monte Carlo (RMC) modeling to obtain structural models from the cryo-ePDF data. From these model structures, we derive structural metrics including stoichiometry, pair distances, and coordination environments in the ALD films and ALD-modified interfaces. The cryo-ePDF technique can be used for routine measurement of atomic structure with high spatial resolution to improve understanding of ALD materials, establish structure-property relationships, and help accelerate the timescale for the application of ALD to address technological needs.

AF9-11 Growth and Characterization of Sodium Fluoride Thin Films Deposited by Atomic Layer Deposition, ***Sara Kuraitis***, Boise State University*; D. Kang, A. Mane, H. Zhou,* Argonne National Laboratory*; J. Soares,* Boise State University*; J. Elam,* Argonne National Laboratory*; E. Graugnard,* Boise State University

Control over the interface between electrolytes and electrodes is key to improving the performance of lithium and sodium ion batteries. Atomic layer deposition (ALD) has attracted interest as a promising approach to the deposition of conformal, pinhole-free thin films on anodes and cathodes in rechargeable battery systems. Such coatings must be stable, prevent dendrite formation, allow for ion conduction, and, ideally, extend cyclability and lifetime. ALD of LiF has shown promise for Li-ion battery systems, and here we report an ALD process for sodium fluoride (NaF) thin films using a similar chemistry. NaF growth experiments were carried out using sodium *tert*-butoxide and HF-pyridine temperatures between 175 and 250 °C. The resulting cubic polycrystalline NaF films exhibited nearly stoichiometric composition (Na:F = 1:1.05), low roughness (Rq ≈ 1.6 nm for ~8.5 nm thick films), and a growth per cycle value of 0.85 Å/cycle on SiO_2 substrates and 3.2 Å/cycle on Al_2O_3. Application of conformal ALD NaF films to battery electrodes may hold promise for improved performance in rechargeable battery systems.

AF9-14 Advanced Applications of Noncontact Electrical Metrology for ALD Films and Interfaces, ***Marshall Wilson***, *D. Marinskiy, J. Lagowski,* Semilab SDI

The noncontact charge-based metrology adopted from the silicon industry enables wafer level, very precise electrical characterization without fabrication of any test devices or contaminating contacts. The key advantages are the low cost and rapid feedback that shall benefit the novel implementations of ALD films.

Two different, new applications presently discussed include: 1. characterization of Al_2O_3 and AlN films on wide bandgap AlGaN and GaN structures for HEMT technology; and 2. a unique charge-induced, noncontact ferroelectric poling and characterization of ALD HfO_2 on silicon.

Noncontact metrology employs precise dosing of charge, ΔQ_C, on ALD film surface, performed with a corona discharge in air.The surface charge provides an electrical bias in analogy to gate bias. The response is monitored as a change of the surface voltage, ΔV, measured with a noncontact Kelvin probe. The differential capacitance $C=\Delta Q_C/\Delta V$ is determined, and corresponding C-V and C-Q characteristics provide a means for extraction of parameters characterizing ALD films, and the film/substrate interfaces, including 2DEG. Results are presented for a skew of thermal ALD AlN films with varying ALD cycles on standard, normally on AlGaN/GaN HEMT structures.

The metrology also includes high charge, time resolved SASS voltage technique for direct determination of a dielectric film thickness. For the AlN skew a linear thickness dependence is seen above 50 cycles. However, the growth is slower for 20 cycles. The latter may be an indication of the growth incubation effect analogous to thermal ALD AlN on silicon substrates. ALD films in the HEMT multi-layer structure may be difficult to model in ellipsometry measurements. The direct SASS technique offers an advantage.

For noncontact measurement of ferroelectric Si doped HfO_2, it is critical that the high charge density SASS pulses provide a noncontact means for poling of the film. A subsequent small charge incremental capacitance measurement gives hysteresis characteristics and "butterfly" permittivity curve. In recently introduced metrology, the ferroelectric poling-measuring sequence is fully automated. As demonstrated by results for 4% Si doped ALD HfO_2, such measurement gives the ferroelectric characteristics and the ferroelectric parameters that also includes the maximum capacitance and polarization charge.

The wafer testing includes initial surface voltage mapping. This high speed, 2 min per wafer screening, is a powerful means for evaluation of wafer uniformity after ALD growth.

AF9-17 Assessing the Quality of 3D-printed ALD Films by Low Energy Ion Scattering, ***Philipp Brüner***, IONTOF GmbH, Germany*; I. Kundatra, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; T. Grehl,* IONTOF GmbH, Germany

Miniaturizing a spatial ALD reactor for integration into a small print head enables 3D-printing of ALD films in arbitrary patterns on large areas of many cm² by lateral movement of the substrate. The lateral resolution, or line size, of 400 µm is given by the size of the print head, while the vertical resolution is determined by the ALD process employed, ideally reaching atomic layer resolution [1].

In this study, we use Low Energy Ion Scattering (LEIS) to assess the quality and the properties of the deposited films. With its high surface sensitivity of just a single monolayer, the ability to measure film thickness, and the quantitative determination of the elemental composition, LEIS elucidates the lateral homogeneity of the printing process with regards to film thickness, surface coverage, and film composition. The selectivity of the deposition is another important aspect. Naturally, any printed pattern comprises growth areas and non-growth areas, and the print head must be designed in a way to provide maximum selectivity between these areas. Good detection limits in combination with the high surface sensitivity allow LEIS to pick up trace amounts of deposited material on the non-desired areas, such that the selectivity is determined quantitatively.

The samples analyzed include line patterns for testing purposes, consisting of Pt and TiO_2 films, and the ATLANT 3D company logo printed with Pt (fig. 1). While LEIS is normally used as an averaging technique, with analysis areas of a few mm², this type of sample requires a pixel-resolved analysis by scanning the analysis ion beam. We show how the data obtained is evaluated to address the analytical questions outlined above. The LEIS surface scattering signal shows that the Pt film only reaches full coverage in the thicker parts of the film (fig. 1), which is an indication for the growth of individual particles instead of flat films. Excellent selectivity for the deposition of Pt is found, with a lower bound of at least 100,000 (ratio of material deposited on growth area vs. non-growth area).

Analyzing the sub-surface LEIS signal originating from ion scattering processes below the surface allows determining film thickness up to a few nm in a laterally resolved way. We also show how LEIS distinguishes between different film compositions, in this case pure Pt and PtO_x films.

AF9-20 Resistive Switching Performance of Mixed Al_2O_3 and ZrO_2 Thin Films, ***Joonas Merisalu***, *T. Jõgiaas, A. Kasikov, A. Tamm, J. Aarik, K. Kukli,* University of Tartu, Estonia

In the search for resistive switching (RS) media, mixing dielectric materials is widely practiced, taking advantage of versatile possibilities of atomic layer deposition (ALD). There are some studies on RS of ZrO_2 as the host dielectric oxide [1,2], and few papers have reported RS of ALD-grown ZrO_2:Al_2O_3 mixtures [3] or nanolaminates [4]. In the present study, ZrO_2:Al_2O_3 films were grown on TiN bottom electrodes to thicknesses 10–15 nm by ALD using $Al(CH_3)_3$, $ZrCl_4$ and H_2O as precursors at 300 °C, whereas earlier $AlCl_3$, as a precursor less prone to thermal decomposition has been applied in the processes [3,4]. In the present study, the ZrO_2:Al_2O_3

cycle ratios ranged from 24:1 to 4:1 yielding Al:Zr cation ratios 0.04–0.4. The RS structures with Ti-Au top electrodes demonstrated multiple clockwise bipolar RS with low to high resistivity window over 5 orders of magnitude in the conductivity scale (Fig. 1), clearly exceeding that observed earlier [3,4], while some samples demonstrated multilevel RS (Fig. 1). The forming voltage, though, was rather high ranging from 4 to 6 V. Interestingly the forming took place under positive voltage applied to Ti-Au electrode which is more common for counterclockwise RS. The effects of cycle ratios and sequencing on the crystalline structure, switching polarity and low to high resistivity ratios will be discussed.

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