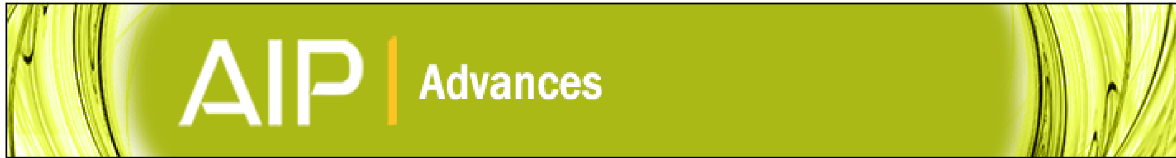

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Vacuum ultraviolet photochemical selective area atomic layer deposition of Al_2O_3 dielectrics

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We report the photochemical atomic layer deposition of Al_2O_3 thin films and the use of this process to achieve area-selective film deposition. A shuttered vacuum ultraviolet (VUV) light source is used to excite molecular oxygen and trimethyl aluminum to deposit films at 60°C. In-situ QCM and post-deposition ellipsometric measurements both show that the deposition rate is saturative as a function of irradiation time. Selective area deposition was achieved by projecting the VUV light through a metalized magnesium fluoride photolithographic mask and the selectivity of deposition on the illuminated and masked regions of the substrate is a logarithmic function of the UV exposure time. The Al_2O_3 films exhibit dielectric constants of 8 – 10 at 1 MHz after forming gas annealing, similar to films deposited by conventional thermal ALD. © *2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4905887]

I. INTRODUCTION

Conventional atomic layer deposition (ALD) is a thermo-chemical process whereby pairs of reagents are sequentially pulsed in cycles onto a heated substrate. The combination of the substrate temperature and the chemical reactivity of the precursors drives the process forward to deposit thin films layer-by-layer. Because the process occurs on the surface and is self-limiting, highly uniform and conformal layers can be deposited with ultra-precise thickness control, even onto high-aspect ratio or porous materials. As an alternative to substrate heating, various forms of other "energy – enhanced" ALD processes have been previously reviewed[1] including plasmas and light enhanced ALD. The use of light to stimulate ALD growth may be either thermal or photo-chemical in nature. The advantage of photo-driven ALD is cited as higher growth rates coupled with the need for less heat input from the substrate heater. Despite these apparent advantages, very few reports of photo-assisted atomic layer deposition (ALD) have been made. For example, tantalum oxide thin films have been deposited by photo-assisted ALD using $Ta(OC_2H_5)_5$ and H_2O as precursors[2] excited by 185 nm ultraviolet (UV) illumination. The relative growth rates per cycle (GPC) for the conventional thermal ALD and photo-assisted processes were 0.42 Å and 0.47 Å respectively. The photo-enhancement was attributed to an increase in surface reactivity and faster surface reaction kinetics. A UV (254 nm Xe lamp) - enhanced ALD process has also been reported for the deposition of ZrO_2 thin films on poly (ethylene terephthalate) substrates using zirconium(IV) tert-butoxide and H_2O precursors.[3] The enhancement from UV irradiation was ascribed to an improvement of the dielectric properties of the oxide and its adhesion to the polymer substrate. The effect of UV irradiation ALD TiO_2 has been reported to increase the growth rate of anatase by a factor of 2 (~ 0.25 nm/cycle), which was thought to arise from a light-induced increase in the density of chemisorption sites.[4] To date, these photochemical ALD processes have not been exploited to manufacture patterned films. The field of area selective ALD processes is being widely developed and has been recently reviewed.[5] These include conventional photolithographic (e-beam or UV)

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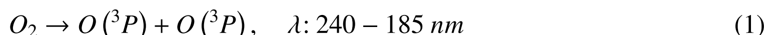
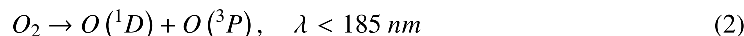
patterning of a sacrificial resist, followed by chemical etching or lift-off to transfer the pattern into the ALD film. Another approach is the use of patterned adsorbates or self-assembled monolayers to enhance[6] or suppress[7] subsequent atomic layer deposition. So-called 'direct write' using focused electron-[8] or ion-beams[9] have also been used to stimulate localized atomic layer deposition. In this paper, we report the photochemical deposition of ALD alumina thin films and demonstrate selective area deposition through the combination of UV irradiation and a photomask.

A conventional ALD reactor geometry was adapted to incorporate a switchable ultraviolet source. The optical train consists of a deuterium – hydrogen VUV lamp; a pneumatically activated shutter; and a UV transparent magnesium fluoride photolithographic mask. ALD is amenable to very small working spaces above the growing film surface, because of the pulsed delivery mode and the lower overall operating temperatures, hence it is possible to use masks in a "virtual contact" configuration with working distances from a few millimeters down to 100 μm or less. The shutter is closed during the precursor dosing cycle to protect the VUV source window from unwanted deposition. For these experiments, the output from the VUV lamp (Hamamatsu, model L11798/-01) has a spectral range from 115 to 400 nm and was configured to photo-chemically decompose the gas-phase precursors both above the surface and as adsorbates on the surface to form the film. The light source has peak emissions in this range of 125 nm (9.9 eV) and 160 nm (7.7 eV). The reactor is run at a pressure of 0.1 Torr with the mask positioned 250 mm away from the light source and a working distance of 500μm – 100μm between it and the silicon substrate. The deposition of alumina was chosen as a model system to explore the effect of photochemical excitation on the growth mechanisms, from trimethyl aluminum (TMA, SAFC Hitech). The photochemical ALD of alumina has been studied at 60°C in order to suppress the growth by the thermally driven process. Molecular oxygen (20 sccm, BOC research grade) is used instead of water vapor, as it has a high radiation absorption cross-section of $\sigma = 4.97\times10^{-18}$ cm^2 (@ 160 nm)[10] in the range of the vacuum ultraviolet source used here and because it does not react with TMA while in its molecular form at 60°C. The gas phase reactions of O_2 with VUV radiation are dominated by the processes:



$$O_2 \rightarrow O\left(^3P\right) + O\left(^3P\right), \quad \lambda: 240 - 185\,nm \tag{1}$$



$$O_2 \rightarrow O\left(^1D\right) + O\left(^3P\right), \quad \lambda < 185\,nm \tag{2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{3}$$

where the atomic oxygen forms triplet (O(^{3}P)) or singlet (O(^{1}D)) electronic states and M denotes a third body. The O(^{3}P) species has two unpaired electrons, which makes it reactive to chemical reactions such as hydrogen abstraction from other molecules. A quartz crystal microbalance (QCM) was used to monitor the mass change occurring during the ALD process as a function of time, which is shown in Fig. 1(a). The QCM frequency response was used to calculate the mass change (Δm) using the procedure developed by Rahtu et al.[11] The inset in Fig. 1(a) shows the mass gain occurring within a single ALD cycle. Each cycle consisted of a 0.02 s TMA exposure / 5 s purge / 10 sec O_2- VUV exposure / 5 s purge. At the start of each super cycle, the initial short TMA pulse (0.02 s) floods the reactor with precursor causing deposition on the crystal and an associated mass gain. Subsequently when the UV shutter is opened (10 s), with O_2 flowing, a mass loss is observed followed by a mass recovery before the next TMA pulse. The same effect has been observed in QCM studies of Al_2O_3 deposition using TMA and ozone (O_3) at 70°C and 205°C.[12] The authors suggest that the O_3 causes O atom insertion into Al–C and C-H bonds converting the methyl species into methoxy (-OCH_3), formate (-OCHO), carbonate and hydroxyl surface species, with the amounts of each being dependent on temperature and ozone exposure. At low temperature, 70°C, the authors[12] reported a small mass gain following the ozone exposure, attributed to the formation of methoxy and formate species on the surface. However, at 205°C, they report a small mass loss and attributed this to ozone's ability to oxidize and hence remove the surface surface carbon species in this temperature region. Ozone is an active oxidant for ligand removal via the formation of ethene (C_2H_4), carbon monoxide (CO) and carbon dioxide (CO_2). In the current study, we observe a mass loss consistent with the 205°C data in Ref. 12 even though the substrate temperature used here is only 60°C. It is postulated that the VUV not only generates an ozone concentration in-situ above the growing film, but also provides photoexcitation to drive forward the oxidation process required

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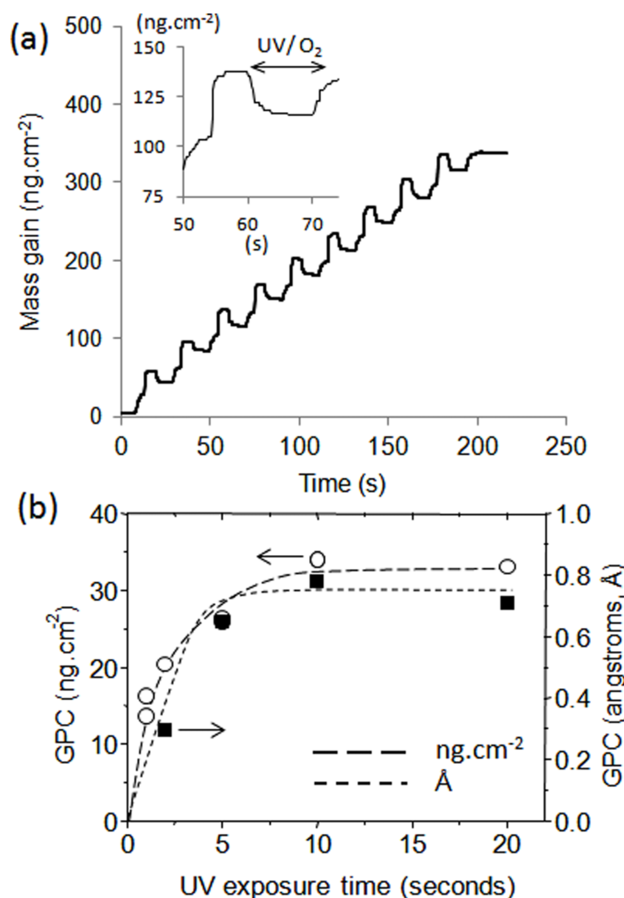

FIG. 1. (a) Mass change versus time for a series of ALD cycles of TMA and UV/O_2 exposure at 60°C. (b) Growth per cycle as a function of UV exposure time measured by the QCM mass gain and ellipsometry.

for effective elimination of the surface carbon species. Fig. 1(b) shows the growth per cycle (GPC) derived from the QCM data and also separately from single wavelength (633 nm) ellipsometry measurements made on silicon (100) samples exposed to the same growth conditions. Both data sets indicate that as the VUV illumination time is extended beyond 5 s to 10 s the overall mass gain per cycle saturates and becomes approximately constant, which is consistent with other self limiting ALD processes. Previous low temperature ALD studies of Al_2O_3[12] with TMA and either ozone or water[13] indicate mass gain rates of 30 – 40 ng.cm^{-2} per cycle are typical under saturative growth conditions. Hence, the GPC data shown in Fig. 1(b) as a function of UV exposure is consistent with the conventional thermal ALD process. The ellipsometry data was corrected for the presence of an initial native silicon oxide (18 Å) which yielded an ALD Al_2O_3 growth rate per cycle at saturation of 0.7 Å/cycle. This figure is lower than the typical value of 1.1 Å/cycle of alumina from TMA and water at 200°C deposited in our laboratory, however it is commensurate with previous growth studies using TMA and O_3 at lower temperatures.[12]

One motivation for using UV irradiation to stimulate a photochemical ALD process is the prospect of realizing area-selective deposition via a photolithographic approach employing a physical mask to "direct write" the ALD film under illumination. Figure 1 indicates that the duration of UV exposure clearly influences the life time of the ozone generated in-situ. From this observation, it is expected that the precursor flow regime will have an effect on the ozone distribution and consequently the selectivity of photochemical ALD that can be achieved. To assess this effect, a photolithographic mask was used to investigate area-selective deposition via UV illumination. In order to avoid the absorption of the VUV in a conventional fused silica-based photolithographic mask (cutoff ~ 200 nm) a simple contrast mask was fabricated using a 1 mm thick magnesium

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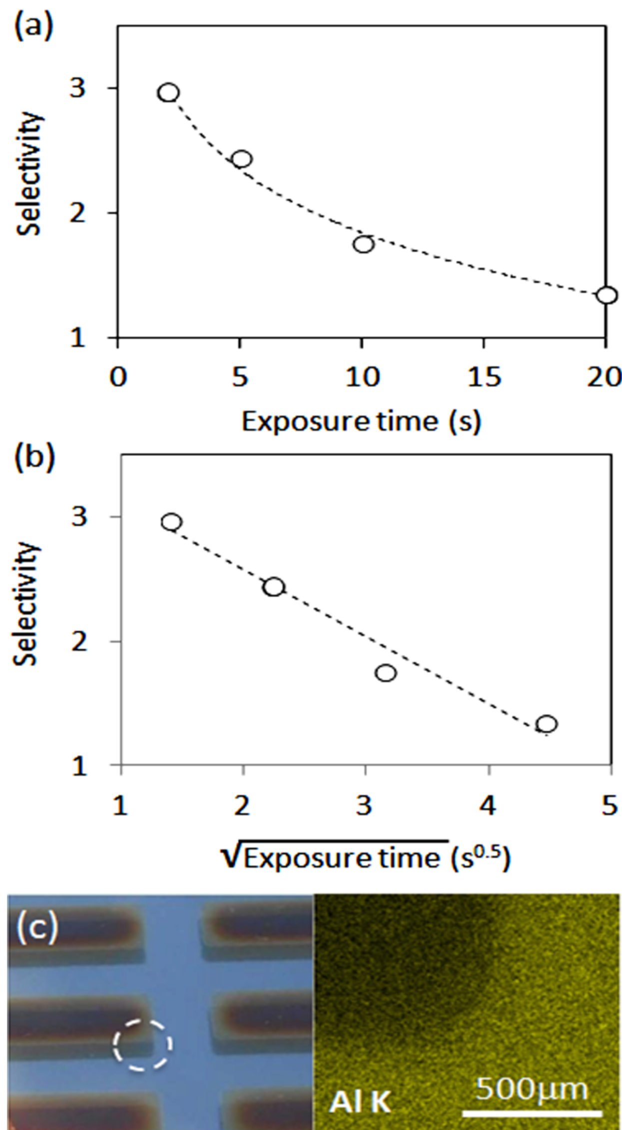

FIG. 2. (a) Contrast ratio of deposition in the illuminated and masked regions as a function of UV exposure time for a mask – substrate separation of 500μm. (b) Contrast ratio versus (exposure time)$^{0.5}$. (c) Picture of the mask and area producing the patterned aluminum distribution in the adjacent Al Kα energy dispersive X-ray map.

fluoride (MgF_2) disc, coated with a patterned 100 nm thick sputtered silver metallization layer to block UV transmission. The mask was supported 500 μm above the silicon (100) substrate for these experiments. Ellipsometry was employed to measure the Al_2O_3 film thickness deposited under the mask aperture and in the masked substrate regions. The selectivity of deposition was assessed using the ratio of deposition in the illuminated and masked regions, as shown in Fig. 2(a) as a function of UV exposure time. With a mask – substrate separation of 500 μm, 2 second exposure times, results in a selectivity of up to three, however at longer exposures the ratio decreases logarithmically. A plot of selectivity versus the square root of exposure time (Fig. 2(b) shows a linear relationship, which suggests a gas phase diffusion process is responsible for deposition in the masked area during the oxygen photo-excitation. The selectivity of the process effects the definition of the ALD features deposited. This can be readily seen using energy dispersive x-ray analysis to map the aluminum distribution of the selectively deposited Al_2O_3 using a 2 second UV exposure. Figure 2(c) shows a picture of the mask region which generated the Al distribution observed in the adjacent image. The

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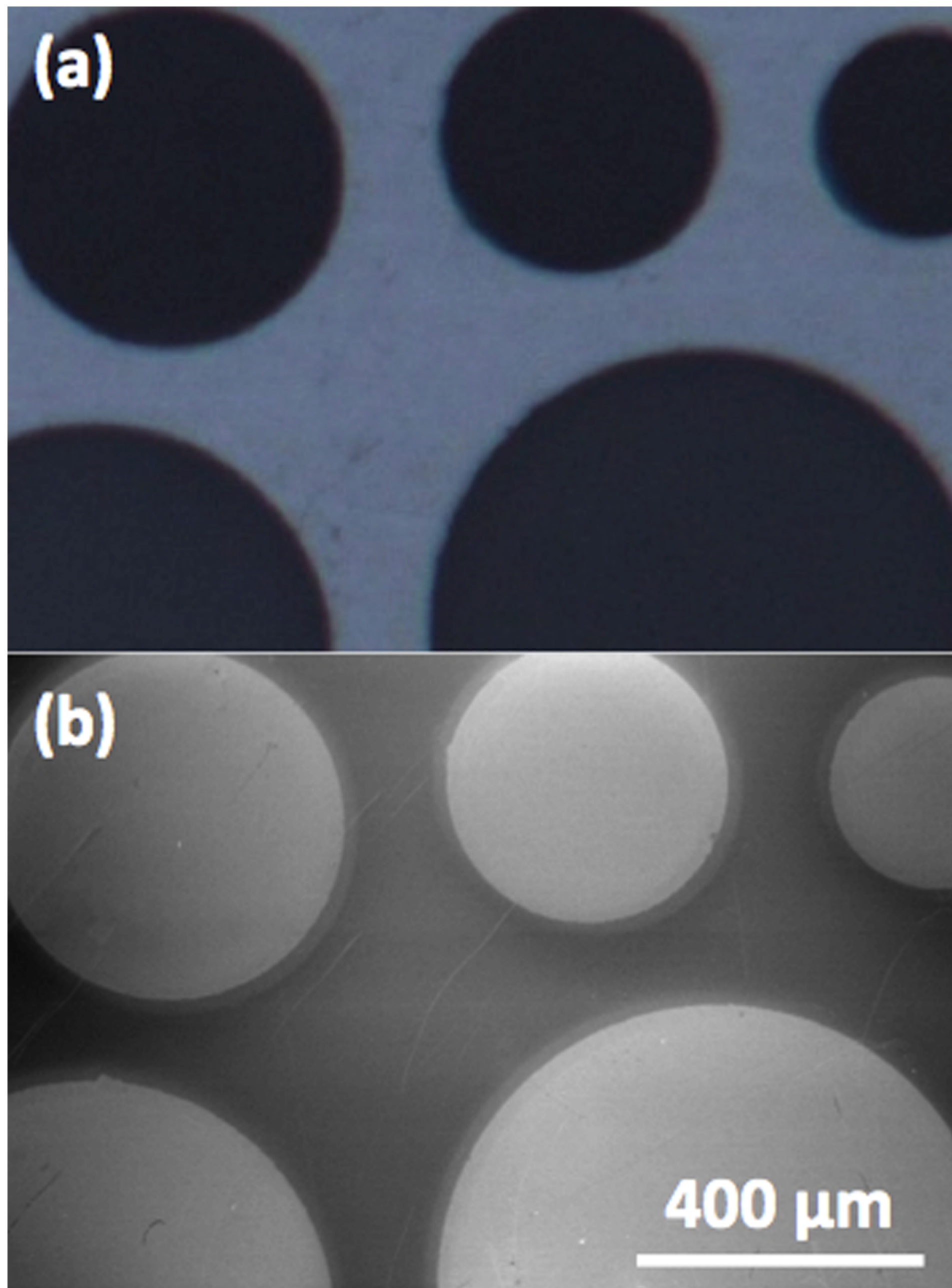

FIG. 3. (a) Optical micrograph of lithographically patterned silver on MgF_2 mask; (b) Secondary electron image of area-selective photochemical ALD Al_2O_3 deposited with a mask – substrate separation of 100μm.

aluminum energy dispersive X-ray Kα map (5 kV beam, 11 nA) shows the resulting delineation between the deposited film and the masked substrate region. The background deposition in the masked region is attributed to the mobility of the ozone between the mask and substrate.

To enhance the area-selective deposition the mask – substrate separation was reduced to a gap of ∼100 μm and a stop valve was employed during the UV exposure step in the ALD cycle to minimize the gas flow regime. A second MgF_2 mask was fabricated with circular apertures of various diameters, shown by the optical micrograph in figure 3(a). This mask was used to selectively deposit Al_2O_3 on silicon using 5 s UV illumination per cycle. An electron micrograph of the sample after deposition is shown in Fig. 3(b), demonstrating that the deposited film pattern closely replicates

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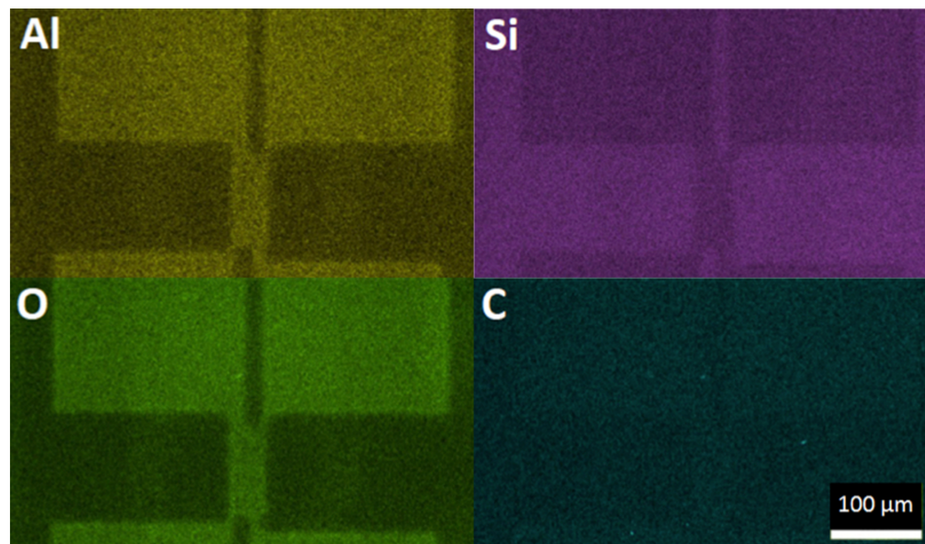

FIG. 4. Energy dispersive X-ray maps of the Al Kα, Si Kα, O Kα and a C Kα distributions from of a photochemical ALD Al_2O_3 test structure deposited with a mask – substrate separation of 100µm.

the pattern of mask. The composition of the selectively deposited Al_2O_3 was investigated using energy dispersive x-ray analysis. Figure 4(a) shows energy dispersive X-ray Kα maps (5 kV beam, 11 nA) of the aluminum, silicon, oxygen and carbon distributions of a test pattern, which indicate the contrast between the regions of enhanced (illuminated) and suppressed (masked) growth. The illuminated regions of the Al_2O_3 test pattern clearly show enhanced regions of Al and O, correlated with the suppression of the underlying Si signal. Negligible carbon from the Al_2O_3 film was observable by EDX, although the low atomic number of carbon limits the detection of carbon to 0.5 – 1 at% with the detector used. The dielectric properties of ALD Al_2O_3 have been extensively characterized and an effective measure of the compositional integrity of the photochemical ALD alumina thin films can be gained from their permittivity. Samples of the selectively deposited Al_2O_3 were fabricated into [$Au/Al_2O_3/SiO_2/Si/Al$] MOS capacitors and their capacitance-voltage (C-V) characteristics were measured after forming gas annealing at 430°C. The relative permittivity (κ) values extracted from accumulation were 8 - 10 at 1 MHz for both materials which is similar to ALD Al_2O_3 deposited by conventional processes.

In conclusion, vacuum ultraviolet irradiation has been used to promote Al_2O_3 film growth via an atomic layer deposition approach. The UV irradiation excites the oxygen co-reagent to generate reactive ozone in-situ and QCM measurements show similar mass gain / loss mechanisms to Al_2O_3 grown with trimethyl aluminum and ozone by ALD at higher temperatures. The in-situ photo-excitation process has been exploited to selectively deposit the dielectric by exposing the patterned film through a magnesium fluoride based photolithographic mask.

ACKNOWLEDGEMENTS

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