Tracing the plasma interactions for pulsed reactive crossed-beam laser ablation

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Pulsed reactive crossed-beam laser ablation is an effective technique to govern the chemical activity of plasma species and background molecules during pulsed laser deposition. Instead of using a constant background pressure, a gas pulse with a reactive gas, synchronized with the laser beam, is injected into vacuum or a low background pressure near the ablated area of the target. It intercepts the initially generated plasma plume, thereby enhancing the physicochemical interactions between the gaseous environment and the plasma species. For this study, kinetic energy resolved mass-spectrometry and time-resolved plasma imaging were used to study the physicochemical processes occurring during the reactive crossed beam laser ablation of a partially ¹⁸O substituted La_{0.6}Sr_{0.4}MnO₃ target using oxygen as gas pulse. The characteristics of the ablated plasma are compared with those observed during pulsed laser deposition in different oxygen background pressures. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934553>]

I. INTRODUCTION

Pulsed reactive crossed-beam laser ablation (PRCLA) is a well-established and effective method to enhance the chemical activity in a plasma during the ablation of a target.^{1–12} Instead of setting a constant background pressure, as typically done for pulsed laser deposition (PLD), PRCLA uses a gas injected through a piezo-controlled nozzle near the ablated area of the target.^{1,2,5} By triggering the gas pulse with the appropriate delay time with respect to the laser pulse, it is possible to set a strong pressure gradient along the direction of the expansion of the ablated plasma plume. In particular, a relatively high local partial pressure can be achieved at the origin of the ablated plasma, promoting physicochemical interactions between the ablated plasma and the gaseous environment. Unlike for standard PLD, the partial pressure in PRCLA between target and substrate drops very quickly and the ablated plasma after crossing the relatively high pressure region expands essentially in a low background pressure. As a consequence, the probability of further interactions (dissociation of metal-oxygen (MO) ions, neutralization of charged species) is highly suppressed. PRCLA is conducted in vacuum or in combination with a constant background pressure up to 0.1 Pa, and gases different to the background environment can be used including highly reactive gases such as NH₃ due to the required very small effective volume.^{2,11,12}

Several successful applications of PRCLA have been reported to fabricate thin films of CuO, AlN, GaN, Ti:Al₂O₃, TiC_xN_y, and SiC using gases such as O₂, N₂O, NH₃, N₂, and CH₄.^{1,3,4,6} Furthermore, PRCLA was also used to complement the standard PLD method in order to enhance the oxygen content in a film^{7–10} or to change the anionic composition of an as-deposited oxide material. Using NH₃ as the

injected reactive gas, the photocatalytic active oxynitride LaTiO_{3–x}N_x can be directly deposited from a La₂Ti₂O_{7–x} target.^{11,12} Nevertheless, there is still very limited information available on the chemical and physical properties between the reactive gas pulse and the ablated plasma plume.^{2,8}

Here, we report on the chemical composition and expansion profile of the plasma plume of La_{0.6}Sr_{0.4}MnO₃ (LSMO) using kinetic energy resolved mass spectrometry and time as well as wavelength resolved plasma imaging. To trace the origin of the oxygen for plasma species and in thin films, the LSMO target was partially substituted with ¹⁸O₂ (~52%), while oxygen with the natural isotopic ratio was used for the gas pulse and the background pressure. The relative content of the different ionic species detected in the plasma as well as the plasma spatial distribution during PRCLA have been compared with results obtained with standard PLD in vacuum and in different oxygen background pressures.

II. EXPERIMENTAL

A La_{0.6}Sr_{0.6}Mn^{16/18}O₃ cylindrical ceramic target was ablated using a KrF laser with $\lambda = 248$ nm and a fluence of 1.8 J/cm². Pulsed reactive crossed beam laser ablation was performed using oxygen for the pulsed gas jet provided by a piezo-controlled nozzle placed in the same plane as the laser spot, next to the ablated target surface. The piezoelectric pulsed valve is used to generate a pulsed supersonic jet expansion into vacuum with an injection pressure of 2×10^5 Pa at the nozzle. Starting from vacuum, the injection of the triggered pulsed gas jets resulted in an average oxygen partial pressure of about 0.02 Pa. The piezoelectric valve was triggered with the laser pulses by setting an opening time of 500 μ s and adding a tunable delay between 100 and 900 μ s with respect to the laser pulses. Pulsed laser deposition was performed in the same deposition chamber in vacuum and in different oxygen background pressures between 0.2 and

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10 Pa. More details to the experimental setup are described in Refs. 2, 5, 8, and 12.

The composition and content of the ionic plasma species were analysed using an electrostatic quadrupole mass spectrometer (Hidden analytical EQS). In addition, time resolved plasma imaging (Andor Solis USB iStar) combined with an acousto-optical tunable filter (AOTF) (Brimrose VA210-.40-.65-H) was used to study the time-resolved spatial distribution of selected excited species. The images are obtained by tuning the AOTF to a specific wavelength for one excited species in the range between 400 and 650 nm with a spectral resolution of 0.8 and 2.1 nm. The plasma imaging was performed at different delay times with respect to the laser pulse using an adjustable gate width for the image acquisition. A photodiode excited by the ablating laser beam provided the signal used to trigger the mass spectrometer and the CCD camera for plasma imaging after adding the suitable delay times.

The film deposition was performed using the same experimental setup by replacing the mass spectrometer with the substrate holder at the same target-substrate distance. (001)-oriented Si substrates were used for the deposition at room temperature and (001) SrTiO₃ for the deposition at 650 °C by measuring the substrate temperature with a pyrometer. The as-deposited films were cooled to room temperature without changing the vacuum conditions for the ablation. To determine the out-of-plane orientation of the as grown films, the structural analysis was conducted at a Siemens D500 x-ray diffractometer with a standard detector unit. For the chemical composition analysis, a detailed Rutherford back scattering (RBS) analysis was done while Elastic Recoil Detection Analysis (ERDA) was used to separate the ¹⁶O and ¹⁸O isotopes.

III. RESULTS AND DISCUSSIONS

The most distinctive feature of PRCLA is a large pressure gradient between the injection nozzle and the substrate during ablation² in contrast to a uniform background pressure in which standard PLD takes place.¹ The time required for the injected oxygen molecules to cover the distance between target and substrate is about two orders of magnitude longer than the typical time required in vacuum by the ablated plasma to travel the same distance.² Therefore, to

fully exploit the chemical activity of PRCLA, a careful tuning of the opening time of the injection nozzle with an appropriate delay time for each laser pulse is required.

An optimized delay time of 400 μs was determined using mass spectrometry during the growth of TiN thin films from a Ti target and a nitrogen gas pulse.² Figure 1 shows the results of time dependent spatial imaging measurement performed in vacuum. For the presented experiments, excited O⁺ species are selected (OII, emission line: 495.6 nm) which are mainly formed by collisions between the generated plasma species and the gas pulse molecules. The optimum delay time was estimated by imaging the spatial distribution for various delay times between the start of the oxygen gas jet and the laser pulse (200–700 μs) using a constant opening time of 500 μs of the injection nozzle. Each frame was recorded with an exposure time of 200 μs for each laser pulse and 100 accumulations using the laser pulse as a trigger signal. The largest re-excitation of plasma species is due to the interaction with the gas pulse molecules while ablating the target materials within the last 100 μs of the 500 μs opening time of the injection valve thereby setting a delay time of about 450 ± 50 μs. The comparison between mass spectrometry and time resolved plasma imaging shows that the latter technique can indeed be used to clearly identify the time interval where the maximum interaction between the plasma and the injected gas jet occurs.

Figure 2 compares the amount of all positive and negative ionic plasma species detected during PLD in vacuum, at two different static O₂ background pressures and during PRCLA using O₂ as pulsed gas jet. As expected, the total amount of detected ionized species in the ablated plasma is much smaller at the highest oxygen partial pressures p (O₂) = 10 Pa than in vacuum as well as at lower p (O₂) or in the case of the PRCLA. This is the consequence of the much higher collision rate that favors both the neutralization of the charged species and the scattering of the plasma species at larger angles outside the detecting area of the mass spectrometer. Among all positive metal-oxygen ions, LaO⁺ presents the largest amount of species due to its much larger dissociation energy (8.9 eV) as compared to SrO⁺ (3.8 eV) and MnO⁺ (2.9 eV). The amount of MO⁺ and O⁺ decreases significantly with increasing p (O₂), which is attributed to their lower stability during background interactions since negative species are easily decomposed at collisions which

FIG. 1. Plasma imaging of OII (emission line: 495.57 nm, 200 μs gate for image acquisition with no delay time) when using various delay times between the pulsed O₂ injection and the laser ablation. The images show the plane of expansion, and the arrow indicates the propagation direction of the plasma from the target to the substrate.

FIG. 2. Overview of the amounts of positive and negative ionic plasma species in the laser induced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{16,18}\text{O}_3$ plasmas in vacuum, using PRCLA and a constant O_2 pressure.

are very frequent at higher pressures.¹³ The reduction in numbers and stability of negative plasma species at a higher background pressure can be seen in the mass spectra in Fig. 2, where O^- is the only negative species detected at 10 Pa. Even at 3 Pa, the number of MnO^- species is approximately 100 times smaller compared to a vacuum ablation.

It can also be observed that the relative content of ionic species containing ^{18}O decreases with increasing $p(\text{O}_2)$. Starting from an almost 1:1 $^{16}\text{O}/^{18}\text{O}$ ratio for the ablation in vacuum (reflecting the amount of isotope substitution in the target as determined using RBS and mass spectrometry during $^{18}\text{O}_2$ loading of the target), only a very small amount of ionic species containing ^{18}O was found in the plasma at $p(\text{O}_2) = 10$ Pa. This is due to an increase of the scattering rate with increasing pressure leading to the dissociation and creation of MO species thereby using the available $^{16}\text{O}_2$ from the background gas. As a result, significantly more MO species with ^{16}O are created at the expense of the ^{18}O isotope.

This effect is also shown in Figure 3(a) where the total amount of La-containing ionic species is compared for the different PLD pressure regimes and PRCLA. The relative content of La^{16}O^+ increases with increasing $p(\text{O}_2)$ at the expense of La^+ and La^{18}O^+ as a result of an increasing number of

collisions of plasma species with the background molecules. In particular, the relative content of metal-oxygen ions increases with increasing $p(\text{O}_2)$ due to an increase in the creation rate with La-oxygen ions that mostly contain ^{16}O . The ^{18}O content, however, significantly decreases since the finite number of ^{18}O atoms from the target become diluted with respect to ^{16}O from the background and the probability to create La^{18}O^+ becomes smaller. This is in contrast to PRCLA: Besides observing a comparable oxidation yield for La ions with standard PLD at 1–3 Pa, the ^{18}O content was found to be very large, even larger than in vacuum.

This finding could be explained by assuming a significantly enhanced physicochemical interaction between the plasma and the pulsed gas jet at the very early stage of the plasma propagation. In this region, an increase in collisions of the ablated species enables the metallic ions to react efficiently with the oxygen species available, including those originating from the target. Therefore, when using PRCLA, the atomic oxygen from the target may also combine with the atomic lanthanum species at the early stage of the plasma propagation thereby forming La^{18}O^+ , which can explain the larger amount of La^{18}O^+ in the mass spectrum when using PRCLA as compared to a vacuum ablation process. Moving

FIG. 3. Comparison of (a) the total amount of La^+ , La^{16}O^+ , La^{18}O^+ ; (b) $\text{MO}^+ / (\text{M}^+ + \text{MO}^+)$ ratios for La, Sr, and Mn.

away from the region near the target surface, the oxygen partial pressure drops dramatically; hence, the probability of further collisions is reduced, thus preserving the amount of oxygen originating from the target. The same effect can be seen in Figure 2, where the content of La^{18}O^+ in the plasma during PRCLA is larger than in vacuum but a significant reduction of the $^{18}\text{O}^+$ (as well as La^+) content has also been measured, suggesting an effective oxidation of the lanthanum ions not only with the gas jet but also with the oxygen ions from the target.

Figure 3(b) shows that the relative amount of MO ions (considering ^{16}O and ^{18}O) evaluated, by calculating the $\text{MO}^+/(M^+ + \text{MO}^+)$ ratios, increases with increasing $p(\text{O}_2)$ for all PLD pressure regimes. For LaO^+ , the increase with increasing $p(\text{O}_2)$ is the most significant one as a consequence of the largest dissociation energy of all MO^+ species which shifts the ratio between dissociation and creation towards creation with increasing background pressure. When using PRCLA, the $\text{LaO}^+/(M^+ + \text{LaO}^+)$ ratio was about 80% and similar to the PLD process at $p(\text{O}_2) = 3$ Pa. For comparison, the $\text{MnO}^+/(Mn^+ + \text{MnO}^+)$ and $\text{SrO}^+/(Sr^+ + \text{SrO}^+)$ ratios when using PRCLA were below 10%. Such a content of MO ions with a smaller dissociation energy could be reached only for an ablation process at $p(\text{O}_2)$ larger than 3 Pa where a dissociation of MO^+ species becomes preferable and values below 5% were measured for $p(\text{O}_2) \leq 3$ Pa.

For the data shown so far, the effective oxidation yield of the metal ions in the ablated PRCLA plasma using O_2 is comparable with PLD performed at an oxygen background pressure of a few Pa. For the same pressure range, most of the oxygen detected as MO^+ species comes from the interaction of the plasma species with the O_2 background, whereas for PRCLA, a significant amount of oxygen originates from the target. This is the consequence of the pressure gradient set by the gas pulse used. The high energy plasma species ejected from the target strongly interact with the O_2 molecules from the gas pulse with a dissociation and creation of species at a very early stage of the plasma propagation. In this region, the metallic ions effectively interact with all available oxygen species including those from the target. Thereafter, the oxygen partial pressure drops dramatically and hence reduces the probability of further collisions. Due to the limited number of potential scattering events possible in the pressure gradient for the dissociation and creation of species as compared to a constant background pressure, more MO^+ species originating from the target can be observed.

An additional important aspect must be taken into account when comparing PLD with PRCLA: The potential influence of the spatial distribution of plasma species with respect to the pressure gradient through which the ablated plasma propagates and the plume expansion takes place.^{2,8} This will have consequences for the final film composition and can be monitored by time resolved plasma imaging where the spatial distribution of the excited plasma species is recorded.^{14–19} Taking the finite wavelength resolution of the AOTF into account, we identified two characteristic emission lines for Sr (SrI , $\lambda = 496.23$ nm) and SrO ($\lambda = 439.96$ nm), which can be clearly resolved.

Figure 4 shows the time-resolved plasma imaging results for Sr and SrO . The data have been recorded for PRCLA and PLD in vacuum, 3 and 10 Pa $p(\text{O}_2)$. The different images were recorded with increasing delay time from 0.6 to 3.0 μs with respect to the laser pulse and a constant exposure time of 200 ns and 100 accumulations. For a direct comparison with literature,^{14–18} white in each picture represents 50% of the largest pixel intensity detected while black represents the lowest pixel intensity.

The images acquired during PLD in vacuum and at a high background pressure are in very good agreement with previously reported data. At 10 Pa, a significant re-excitation of ablated species as compared to vacuum can be observed over a long time interval as well as the presence of a defined shock wave front that confines the plasma during the expansion. In vacuum, the plasma plume is strongly elongated in the direction of the substrate; species are significantly faster than at a higher deposition pressure ($\approx 40\%$); and a much lower yield of re-excitation for metallic Sr can be observed. Moreover, using the same intensity scale, the re-excitation intensity of SrO in vacuum falls already below the detection limit after ≈ 1 μs . At 3 Pa, the

FIG. 4. Time resolved plasma images at various delay times with a 200 ns window for the image acquisition of Sr (SrI , $\lambda = 496.23$ nm) and SrO ($\lambda = 439.96$ nm) for PRCLA compared to PLD with constant oxygen background pressures and vacuum. The images show the plane of expansion, and the arrow indicates the propagation direction of the plasma from the target to the substrate.

expanding plasma has a hemispherical shape and the expansion velocity is reduced by $\approx 60\%$ for Sr as compared to the vacuum deposition, almost halved at 10 Pa and only reduced by $\approx 35\%$ for PRCLA. The main difference of the plasma expansion for PLD with a background pressure as compared to PRCLA is the intensity and duration of the re-excitation at $t > 1.2 \mu\text{s}$. For Sr at $2.4 \mu\text{s}$ and $p = 3 \text{ Pa}$, the signal is still clearly present, whereas for PRCLA, it has almost vanished. The faster decay in the re-excitation intensity for PRCLA is attributed to the pressure gradient, which provides only a limited pressure zone for collisional re-excitations to occur. Beyond this limited pressure zone, the number of collisions drops rapidly and hence the probability for re-excitations decreases. As a consequence, the measured intensity decays more quickly with respect to PLD with a constant background pressure.

During PRCLA, the spatial distribution of Sr and SrO can be divided into three regions. For $t < 1.5 \mu\text{s}$, the expansion resembles closely the plasma dynamics observed at a high oxygen background pressure for standard PLD. An intermediate region is identified between 2 and $3 \mu\text{s}$. In this time window, the yield of re-excitation processes is similar to PLD in vacuum while the spatial distribution for both Sr and SrO looks very similar to the ablation process at a high background pressure. The low yield of re-excitations indicates a relatively low local oxygen partial pressure which reduces the reaction cross section for collisions and chemical reactions. The observed spatial distribution, however, is the result of species travelling through a region with a high local pressure at an early stage of the plume expansion. For $t > 3 \mu\text{s}$ and concentrating on the region near the substrate 4 cm away from the target, the plasma images for PRCLA show features similar to PLD performed in vacuum with the important difference of the presence of re-excited SrO not detected in vacuum.

This qualitative analysis of time resolved plasma imaging reflects the unique pressure environment of PRCLA characterized by a high local pressure at the very early stage of the plasma propagation near the target. This is followed by a dramatic drop of the local pressure while moving away from the target, thereby preserving the properties of the initially expanding plasma crossing the high pressure region.

The variations in plasma properties are expected to influence the composition, crystalline, and physical properties of as-deposited films grown on (001) STO substrate at $T = 650^\circ\text{C}$.²⁰ For epitaxially grown LSMO on (001) STO, a (001) out-of-plane orientation is expected. No measureable diffraction film peaks were detected for films prepared in vacuum or at a low oxygen partial pressure of 0.2 Pa due to an instrumental broadening of the substrate peak. Increasing $p(\text{O}_2)$ from 1 to 20 Pa, a (006) film peak is observed. For a deposition at 3 Pa, a 2θ value of $\approx 47.1^\circ$ was observed, which corresponds to the expected out-of-plane lattice parameter for these LSMO films. The same lattice parameter was measured for films grown by PRCLA²¹ reflecting very similar chemical plasma properties and probably plasma composition as compared to standard PLD at $p(\text{O}_2) = 3 \text{ Pa}$.

The composition of films grown on STO and Si using PRCLA as determined by RBS and ERDA are $\text{La}_{0.6}\text{Sr}_{0.37}\text{Mn}_{0.82}\text{O}_{2.61}\text{O}_{0.26}$ and $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.80}\text{O}_{2.48}\text{O}_{0.29}$,

respectively,²¹ as compared to the nominal target composition $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}^{16/18}\text{O}_3$. Data of the average Sr and Mn content vs. $p(\text{O}_2)$ for $\text{La}_{0.6}\text{Sr}_x\text{Mn}_y\text{O}_{3-\delta}$ films can be found in Ref. 22, where a systematic change in the film composition is reported coinciding with the changes in the scattering properties of the expanding plasma. Both PRCLA prepared films have a high oxygen content but still noticeably smaller than the stoichiometric value of $x = 3.0$. Based on the ^{16}O to ^{18}O isotope ratio, it is possible to estimate that the oxygen from the gas pulse contributes ~ 78 and $\sim 81\%$ of the total oxygen content of the film on Si and STO respectively. It is also clear that these films are Mn and Sr-deficient as compared to films grown at $p(\text{O}_2) \approx 20 \text{ Pa}$.²² The loss of lighter elements using PLD has been reported previously.^{22–25} For PRCLA, the cation deficiency suggests that the pressure equivalent for a deposition at a static pressure is around 1 Pa, whereas for the oxygen content, it would be more in line with either a $p(\text{O}_2)$ lower than 1 Pa or larger than 10 Pa.²² Therefore, the observed cation deficiency for LSMO is putting an upper pressure limit of $\sim 1 \text{ Pa}$ for the high pressure zone next to the target in which the interaction between plasma species and the injected gas molecules occurs. After leaving this high pressure zone, the created species start to expand into a spatial region with a reduced pressure thereby preserving the plasma composition until reaching the substrate. Similar losses of light cation in the film composition were also observed for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ and $\text{La}_{0.66}\text{Ca}_{0.33}\text{MnO}_3$ thin films grown by PRCLA using O_2 or N_2O in either vacuum or in the presence of a background pressure.^{8–10}

The previous paragraph shows the unique potential of PRCLA for a targeted *in situ* chemistry and hence materials property manipulation: A created chemical composition in a local high pressure region can be preserved and hence a film with a specific composition can be prepared which would be difficult to accomplish otherwise. This is unlike conventional PLD, where—in particular, at a higher, static background pressure—the chemical composition of the plasma is changed dynamically due to collisional interactions of plasma and background species until the very end of the plasma expansion before reaching a substrate. The reason is the difference in dissociation energy of the MO species in the plasma which will determine the ratio between dissociation and creation.²² The smaller the MO dissociation energy becomes, the more probable it is that the respective metallic species will arrive preferentially at the substrate site in particular at a high deposition pressure with many scattering events taking place promoting favorably a MO dissociation.

Based on the measurements performed for this study, we show next that PRCLA is an ideal tool to perform *in situ* materials preparation using a reactive environment which is difficult to use otherwise. One prominent example is the preparation of photocatalytic active oxynitrides as thin film where part of the oxygen in the material is replaced with nitrogen.^{11,12} For standard PLD using N_2 as a background gas, the dissociation of N_2 with its triple bond is very hard to achieve (bond energy $> 8 \text{ eV}$). Using NH_3 for the gas pulse instead of N_2 , a very local and highly reactive environment can be created and used for the successful preparation of, e.g., $\text{SrTiO}_{3-x}\text{N}_x$ or $\text{LaTiO}_{3-x}\text{N}_x$,^{11,12} thereby combining

two advantages. First, to obtain a relevant high local reactive gas environment requires a very small amount of the reactive gas at the target while the pressure into the vacuum chamber can be kept relatively small (below 10^{-2} Pa in our experimental setup). This significantly reduces the loading to the pumping system during a high pressure operation and allows an effective as well as safer use of highly reactive gases such as NH_3 . Second, NH_3 and resulting hydrogen species create a reducing environment for the preparation of the oxynitride film by removing oxygen originating from the target. A positive identification of nitrogen-metal species reaching the substrate is still missing.² In case there are nitrogen-metal species, they are expected to be quite stable with bond energies between 4 and 5 eV.²⁶

IV. CONCLUSIONS

Plasma analysis by mass spectrometry and plasma imaging were used to identify the main differences in the physico-chemical interactions occurring during the plasma propagation when using PRCLA and PLD. These measurements confirm that during PRCLA the molecules of the reactive gas (oxygen in this study) are effectively dissociated and positively charged metal-oxygen ions are generated in large abundance at the early stage of the plasma propagation near the target surface. Moreover, the rapidly decreasing pressure along the direction of the plasma propagation preserves the existence of the less stable as-generated metal-oxygen species, as revealed by the significantly enhanced content in the plasma of oxygen species originated from the target and identified in this study by ^{18}O isotope substitution.

This unique pressure environment for the plasma propagation has been mapped by imaging the spatial distribution of excited species, and the effect of the different pressure regimes is consistent with the plasma chemical composition as revealed by mass spectrometry. During PRCLA, in the region near the substrate, we observed a vacuum-like propagation of excited and re-excited oxidized species that would not exist in the case of PLD performed in vacuum since they are generated in the high pressure region localized near the target surface.

When using PRCLA without a static background pressure, the strong negative pressure gradient from the target to the substrate prevents the formation of a shockwave front that confines the plasma during its expansion. This effect is most probably the reason for the loss of the lighter elements which are scattered more effectively while crossing the high pressure region. The same effect is very often an issue for PLD also. To reduce this effect for PRCLA, the injection

pressure for the gas pulse also needs to be treated as an adjustable parameter.

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