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Possibility of $BaTiO_3$ thin films prepared on Cu substrates for embedded decoupling capacitors by an aerosol deposition method

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$BaTiO_3$ thin films were fabricated on Cu substrates at room temperature employing an aerosol deposition method (ADM) for embedded decoupling capacitors with high capacitance densities in the thickness range of 12 to 0.2 μm. From the thickness dependence of their dielectric properties, it was confirmed that $BaTiO_3$ thin films acted like conductors due to high leakage currents or as dielectrics in near a thickness of 1.0 μm. In this thickness range, we suggest that their high leakage current densities resulted from defects in the $BaTiO_3$ thin films. Through SEM observation, it was determined that the high leakage current densities of $BaTiO_3$ thin films were caused by defects such as pores, craters and weakly bonded areas due to large particles and agglomerated particles. To reconfirm the non-uniformity of the thin film due to defects, we reduced the diameter of the upper electrodes from 1.5 to 0.33 mm. As a result, the dielectric properties of $BaTiO_3$ thin films with upper electrodes of 0.33 mm in diameter could be measured first in a thickness of 0.5 μm. The relative permittivity, loss tangent and capacitance densities were approximately 66, 0.026 and 114 nF/cm^2 at 10 kHz, respectively. Therefore, the possibility of thin films for embedded decoupling capacitors with high capacitance density through an ADM process may be proposed.

Key words: Aerosol deposition method, Embedded decoupling capacitor, $BaTiO_3$, Thin film, Leakage current density, Pores, Crater.

Introduction

Recently, electronic devices, such as personal digital assistants and mobile phones, continue to be subjected to the trends of high frequencies and integration of electronic components for miniaturization. However, both a sudden change of current due to high frequencies and an increase of parasitic inductances in wirings by high integration bring about critical problems, such as electromagnetic interference, simultaneous switching noise, etc [1, 2]. Decoupling capacitors with a high capacitance density are widely used as a solution to suppress these electromagnetic troubles. Also, to reduce the effects of parasitic inductances, embedded passive technology (EPT) which can shorten the length of wiring and give high packaging densities has been extensively researched since the existing discrete surface mounting technology is not effective at above 1 GHz because of its structural limits [3-6].

So far, one of the candidates for EPT has been low temperature co-firing ceramics (LTCCs). However, LTCCs still require high temperature processes around 850 °C and have critical problems such as a limitation on low size accuracy due to shrinkage and interdiffusion during firing [7]. In order to get over these problems, a new approach in a low-temperature process is required to realize embedded decoupling capacitors. Taking these circumstances into consideration, we have paid attention to an aerosol deposition method (ADM) which is a room-temperature process for growing ceramic films. Moreover, ADM is a novel process enabling high deposition rates, high density, wide thickness ranges, and heterogeneous junctions for fabricating ceramic films [8].

Based on the International Roadmap for Semiconductors (ITRS 2007), the capacitance density of decoupling capacitors for use requires at least 100 nF/cm^2 [9]. In previous research, some reports have been published on the capacitance density of decoupling capacitors prepared by polymer composites. However, though the relative permittivity of polymer composites is similar to that of aerosol-deposited $BaTiO_3$ films whose value was approximately 100, it is not appropriate for applications at high frequencies due to a limitation of decreasing the thickness of films [10]. Besides, some studies have been reported for $BaTiO_3$ thin films employing ADM but the dielectric properties of $BaTiO_3$ thin films in the thickness range below 1 μm could not be measured.

Although ADM was originally developed for thick film processes, we have attempted to prepare $BaTiO_3$ thin films in the thickness range below 1 μm on Cu substrates by using ADM at room temperature for embedded decoupling capacitors with a high capacitance density [11]. In our previous research, it has been considered that the major cause of conductor-like behavior was high leakage currents owing to field concentrations at the rough interface between the $BaTiO_3$ thin film and the Cu substrate due to collisions of ceramic particles in the thickness ranging from 0.2 to 1 μm [12].

In this study, we suggest that the cause of high leakage

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currents was the non-uniformity of $BaTiO_3$ thin films. As a result of SEM observations, it was found that the high leakage currents were caused by defects in $BaTiO_3$ thin films. Subsequently, we have used a smaller diameter of upper electrodes to reconfirm the non-uniformity of $BaTiO_3$ thin films and the possibility of a thin film process by ADM is suggested.

Experimental Procedure

The ADM is based on shock loading solidification due to the impact of ceramic particles. The details of an ADM apparatus can be found elsewhere [6, 8, 10]. $BaTiO_3$ particles 0.45 μm in average diameter were used as starting powders. $BaTiO_3$ powders became an aerosol in the aerosol chamber by means of a vibration and mixing system. Then the aerosol was carried to the deposition chamber by He gas at a flow rate of 3 L/minute and accelerated through a nozzle. Finally, the $BaTiO_3$ powders were continuously ejected through the nozzle and deposited onto the Cu substrates. The size of the nozzle orifice was $10\times0.4\ mm^2$ and the deposited area was $5\times10\ mm^2$. The distance between the substrate and the nozzle was 10 mm and the working pressure was 40 Torr (5.3×10^2 Pa). The vibration speeds were 200-400 rpm and deposition times were 1-20 minutes. The root-mean-square (rms) roughness of prepared Cu substrates was measured by AFM. The microstructure to confirm the non-uniformity of the $BaTiO_3$ thin films and crystallinity of the $BaTiO_3$ thin films were examined by a scanning electron microscope (SEM) and an X-ray diffractometer (XRD), respectively. For the measurement of dielectric properties, gold upper electrodes 1.5 mm, 1.0 mm and 0.33 mm in diameter were coated using a shadow mask on $BaTiO_3$ thin films by sputtering. Then the magnitude and phase of their impedance were measured from 1 kHz to 1 MHz by an impedance analyzer and their thickness was measured by a surface profilometer.

Results and Discussion

Thickness dependence of the dielectric properties of $BaTiO_3$ films

To investigate the certain thicknesses for which dielectric properties could be measured, $BaTiO_3$ thin films with thicknesses ranging from 12 to 0.2 μm were deposited at room temperature by ADM on Cu substrates whose rms roughness value was approximately 2 nm. From the XRD profiles of the $BaTiO_3$ thin films with thicknesses ranging from 12 to 0.2 μm, it was confirmed that all the fabricated $BaTiO_3$ thin films were crystalline and their crystal systems were cubic with a single perovskite phase. To investigate the thickness dependence of the dielectric properties of the $BaTiO_3$ thin films, the magnitude and phase of the impedance of $BaTiO_3$ thin films with upper electrodes 1.5 mm in diameter were measured by an impedance analyzer. As a result, three types of groups were established such as dielectric, dielectric or conductors-like, conductors-like.

In the first group, it was confirmed that the phase values of their impedance were approximately -90 degree in thicknesses ranging from 12 to 2 μm as shown in Fig. 1(a). So, from the phase of values, it was determined that all the $BaTiO_3$ thin films acted as dielectrics in this thickness range. Then, the dielectric properties and capacitance densities of $BaTiO_3$ thin films were calculated from their magnitude and the phase of impedance, which are summarized in Table 1.

However, in the second group, some regions of $BaTiO_3$ thin films acted as a dielectric and other regions of the thin films acted like a conductor in thicknesses near 1 μm. The phase values of impedance of the thin films acting like conductors, approximately 0 degrees, are shown in Fig. 1(b). In the case of the regions of the $BaTiO_3$ thin films which acted as a dielectric, their relative permittivity, loss tangent and capacitance density were approximately 66, 0.03, 59 nF/cm^2. However, these $BaTiO_3$ thin films were not good enough to apply to decoupling capacitors because of the low capacitance density. Therefore, it was necessary to decrease the thickness of $BaTiO_3$ thin films to achieve the capacitance density higher than 100 nF/cm^2. In the case of the third group, all $BaTiO_3$ thin films acted like conductors in the thickness range below 1 μm.

In order to investigate the major reason why dielectric properties could not be measured, the leakage current densities of the $BaTiO_3$ thin films which acted like conductors were measured. From the measurement of the I-V characteristics of the $BaTiO_3$ thin films, it was determined that the thin films showing conductor-like behavior had high leakage current densities, almost shorting. Their high leakage currents densities were below 5 A/cm^2 at 5 V.

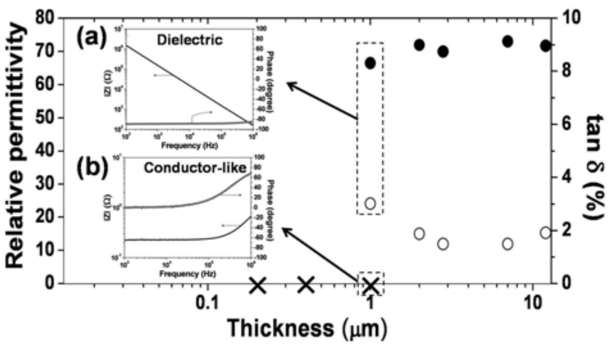

Fig. 1. Thickness dependence of $BaTiO_3$ films in the thickness range of 12 to 0.2 μm and showing the magnitude and phase of the impedance of (a) dielectric (b) conductor-like

Table 1. Dielectric properties according to the thickness of $BaTiO_3$ thin films

	Thickness of films (μm)				
	12	7	3	2	1
ε_r (@10 kHz)	72	73	70	72	66
tan δ (@10 kHz)	0.02	0.015	0.015	0.02	0.03
Cap. density (nF/cm^2)	5.5	9.6	20	35	59

From the above results, we suggest that the high leakage current densities were caused by the existence of defects in $BaTiO_3$ thin films.

At first, we observed optical images of surfaces of all $BaTiO_3$ thin films to investigate the defects which can cause high leakage current densities in the thin films. However, different surface morphologies of $BaTiO_3$ thin films which showed conductor-like or dielectric behavior could not be found. So, to examine defects in the thin films in more detail, we attempted to observe the microstructures of surfaces of $BaTiO_3$ thin films by SEM.

Surface morphologies of $BaTiO_3$ thin films

To investigate the defects which can cause the high leakage currents in $BaTiO_3$ thin films, we observed the surface morphologies of $BaTiO_3$ thin films according to a thickness increase. $BaTiO_3$ thin films with the thickness of 0.2 μm and 1 μm were chosen since $BaTiO_3$ thin films with thicknesses of 0.2 μm showed only conductor-like behaviors and $BaTiO_3$ thin films with a thickness of 1 μm acted conductor-like or as a dielectric in some regions.

In a film with a thickness of 0.2 μm, pores and uniform areas were observed as shown in Figs. 2(a) and (b). The pores existed on the $BaTiO_3$ thin films in several regions and the sizes of pores were 1~5 μm as shown in Fig. 2(a). So, we considered that high leakage currents occurred in the pores which were created due to particles which were larger than the mean particle size or agglomerated particles as shown in Figs. 3(a) and (b). It may

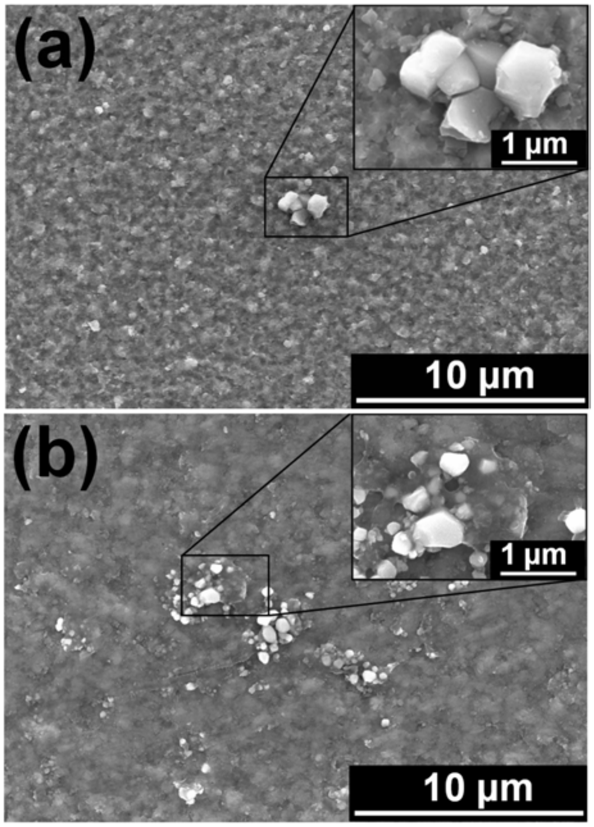

Fig. 3. SEM images of surfaces of $BaTiO_3$ thin films with a thickness of 0.2 μm. (a) Large particles and (b) agglomerated powders on $BaTiO_3$ thin films.

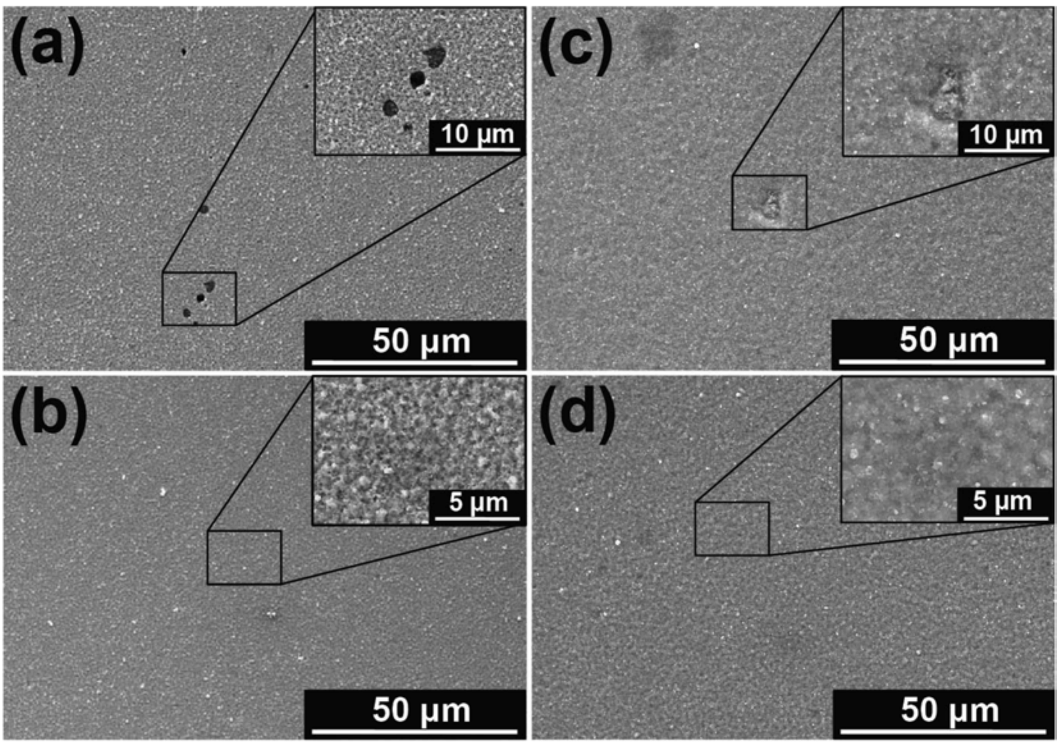

Fig. 2. SEM images of surfaces of $BaTiO_3$ thin films with thicknesses of 0.2 μm and 1 μm. (a) Pores and (b) uniform area on surfaces of $BaTiO_3$ thin films with the thickness of 0.2 μm. (c) The craters (d) uniform areas on surfaces of a $BaTiO_3$ thin film with a thickness of 1.0 μm.

be suggested that the main cause of high leakage currents was the pores. The mechanism of formation of the pores might be summarized as follow. When large particles or agglomerated particles are crushed on surfaces of $BaTiO_3$ thin films, the surfaces of the films became etched by the large particles or agglomerated particles and the pores were created. Therefore, if upper electrodes are coated onto the regions which have pores, the $BaTiO_3$ thin film acts conductor-like due to the high leakage current. In addition, it is suggested that the agglomerated particles created week bonds which created leakage currents in the $BaTiO_3$ thin films because each of these agglomerated particles were not fragmented into smaller pieces. So, almost all the agglomerated particles remained as in a weakly bonded state as shown in Fig. 3(b). Fig. 2(b) shows a uniform area of a $BaTiO_3$ thin films and the area is seen to be very dense.

On the other hand, in the case where the thickness is 1 μm, craters and uniform areas were observed as shown in Figs. 2(c) and (d). It is suggested that the craters were created due to the particles or agglomerated particles which are larger than the mean particle size and these craters are larger than the pores shown in Fig. 2(c). However, the shape of craters was different from those of pores. This may be summarized as follows. At first, the pores were generated by large particles or agglomerated particles. By increasing the thickness of $BaTiO_3$ thin films, the next particles piled up on the surfaces of $BaTiO_3$ thin films. This phenomenon could be confirmed on surfaces of $BaTiO_3$ thin films as shown by comparison Figs. 2(b) and 2(d). So, it is considered that some small pores were filled by the next particles to arrive. However, the other large pores were not on the whole filled. Thereby, craters were created due to the large pores. Therefore, the dielectric properties of some regions of $BaTiO_3$ thin films with a thickness of 1 μm which have craters could be not measured even if the other regions of these $BaTiO_3$ thin films could be measured. Fig. 2(d) shows a uniform area of a $BaTiO_3$ thin film as mentioned above.

Through the observation of surface morphologies of $BaTiO_3$ thin films, it was confirmed that there were three types of defects such as pores, craters, and weakly bonded areas due to large particles and agglomerated particles. It was determined that these defects caused high leakage currents so that $BaTiO_3$ thin films gave conductor-like behavior. In particular, it is considered that the pores had a substantial great influence on high leakage currents.

However, the upper electrodes of 1.5 mm in diameter on the $BaTiO_3$ thin films were relatively large in size even though we tried to confirm the uniformity of $BaTiO_3$ thin films at first. So, a substantial number of defects were contained in the region of the upper electrode so that the dielectric properties of $BaTiO_3$ thin films could not be measured. Thus, it is suggested that if small electrode sizes are coated on dense parts without defects, the same regions of $BaTiO_3$ thin films which showed conductor-like behavior on the whole would act as a dielectric and then an attempt was made to reconfirm the non-uniformity of the $BaTiO_3$ thin films and propose the possibility of a thin film processes by ADM.

Table. 2. Dielectric properties as a function of the diameter of upper electrodes and thickness range of $BaTiO_3$ thin films

Diameter of upper electrodes (mm)	Thickness of films (μm)					
	12~1.3	1.2~1.0	0.8~0.7	0.6~0.5	0.4~0.3	0.2~
ϕ1.5	○	△	×	×	×	×
ϕ1.0	○	△	△	×	×	×
ϕ0.33	○	○	△	△	×	×

○ : Possible to be measured
△ : Possible to be measured partially
× : Impossible to be measured

Dielectric properties according to a decrease in the upper electrode

The dependence of the diameter of the upper electrode on the electrical properties of $BaTiO_3$ thin films was investigated to reconfirm the non-uniformity of $BaTiO_3$ thin films and propose the possibility of a thin film processes by ADM. Upper electrodes with 1.0 and 0.33 mm in diameter were also used. From the measurements of the magnitude and the phase of the impedance of the $BaTiO_3$ thin films with upper electrodes 1.5 to 0.33 mm in diameter, we obtained the dielectric properties of the $BaTiO_3$ thin films as shown in Table 2.

In the case of the upper electrodes 1.5 and 1.0 mm in diameter, the dielectric properties of $BaTiO_3$ thin films began to be measured in films with thicknesses of 1 and 0.8 μm. In particularly, in the case of upper electrodes 0.33 mm in diameter, the dielectric properties of $BaTiO_3$ thin films with a thickness of 0.5 μm could be measured which could not be measured previously. This revealed that small upper electrode regions had few defects so that the dielectric properties of $BaTiO_3$ thin films could be measured. Figs. 4(a) to (c) show their relative permittivity and loss tangent with frequency. The relative permittivity and loss tangent with frequency were approximately 66 and 0.025 at 10 kHz. The capacitance densities of $BaTiO_3$ thin films were calculated from their magnitude and the phase of the impedance as shown in Table 3.

In view of the results so far achieved, we reconfirm the non-uniformity of $BaTiO_3$ thin films by observing the surfaces of $BaTiO_3$ thin films and using small diameter upper electrodes, at the same time, this suggests the possibility of fabrication of $BaTiO_3$ thin films since we measured dielectric properties of $BaTiO_3$ thin films with a thickness of 0.5 μm.

If the particle size distribution of $BaTiO_3$ powders is controlled by an additional process to remove defects such as large particles and agglomerated particles in $BaTiO_3$ powders, it is expected that it will be possible to fabricate embedded decoupling capacitors with high capacitance densities at room temperature for the GHz range by decreasing the thickness of $BaTiO_3$ thin films.

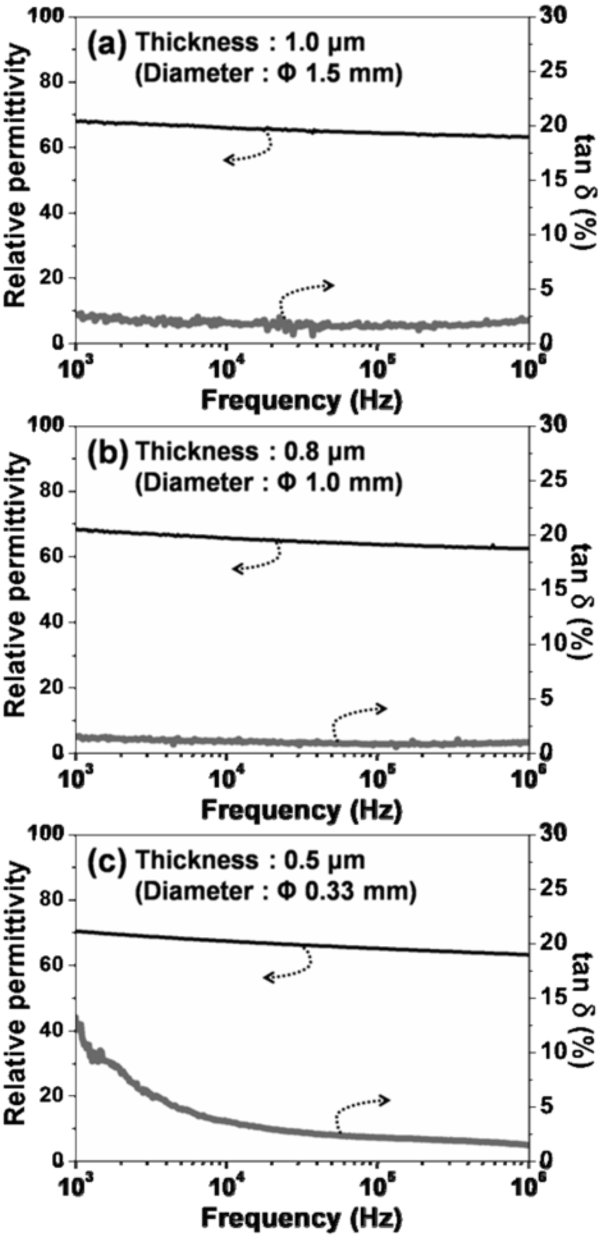

Fig. 4. The relative permittivity and loss tangent dependence of upper electrodes (a) 1.5 mm (b) 1.0 mm (c) 0.33 mm in diameter.

Table 3. Dielectric properties dependence of upper electrodes with 1.5 mm, 1.0 mm and 0.33 mm in diameter.

	Diameter of upper electrodes (mm)		
	ϕ1.5	ϕ1.0	ϕ0.33
Thickness (μm)	1	0.8	0.5
ε_r (@10 kHz)	66	65	66
tan δ (@10 kHz)	0.03	0.025	0.026
Cap. density (nF/cm^2)	59	70	114

Conclusions

For embedded decoupling capacitors with high capacitance densities, the thickness dependence of dielectric properties of $BaTiO_3$ thin films prepared on Cu substrates was investigated in thicknesses ranging from 12 μm to 0.2 μm. With a thickness below 1.0 μm, some parts of $BaTiO_3$ thin films gave conductor-like behavior due to high leakage currents. Through SEM observations of $BaTiO_3$ thin films, it was confirmed that pores, craters which can give high leakage currents. To reconfirm the non-uniformity of the $BaTiO_3$ thin films and investigate the possibility of a $BaTiO_3$ thin films process, the diameter of upper electrodes were changed from 1.5 to 0.33 mm. As a result, the dielectric properties of $BaTiO_3$ thin films with a diameter of the upper electrode of 0.33 mm could be measured in a thickness of 0.5 μm. This suggests the possibility of a $BaTiO_3$ thin film processes by ADM.

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