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SEM and EDS characterization of GaAs layers grown by the close-spaced vapor transport technique at four different geometries using atomic hydrogen as initial reactant

E. GÓMEZ* AND R. SILVA
Instituto de Física "Luis Rivera Terrazas", BUAP
Apartado postal J-48, 72570 Puebla, Pue., México

F. SILVA-ANDRADE
Centro de Investigación en Dispositivos Semiconductores, ICBUAP
Apartado postal 1651; 72000 Puebla, Pue., México

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ABSTRACT. GaAs layers were grown by the close-spaced vapor transport (CSVT) using atomic hydrogen as initial reactant. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to characterize the layers. It is observed that the variation on the experimental setup of the CSVT system and on some growth parameters (spacer thickness and source-substrate temperature gradient) have a remarkable influence on the surface morphology of the grown layers. It is inferred that the stoichiometric deviation presented by all layers under study is due to the interaction of the atomic hydrogen with the source and substrate at high temperatures ($\geq 650°$C) during their growth process. The EDS analysis performed on the layers also shows that the main impurities are Si, O, and C. By an additional experiment, it was proved that the origin of the Si, and O contaminants is the etching effect of the quartz spacer by atomic hydrogen and it is inferred that the origin of the C contaminant is mainly due to some contamination existing in the reactor.

RESUMEN. Se crecieron películas de GaAs por la técnica transporte de vapor a corta distancia (CSVT) usando hidrógeno atómico como reactante inicial. Las técnicas de microscopía electrónica de barrido (SEM) y espectroscopía de energía dispersiva (EDS) se emplearon para caracterizar estas películas. Se observa que la variación en el arreglo experimental del sistema CSVT y en algunos parámetros de crecimiento (espesor del separador y gradiente de temperatura fuente-sustrato) tienen una notable influencia en la morfología superficial de las películas crecidas. Se infiere que la desviación estequiométrica que presentan todas las muestras bajo estudio es debida a la interacción del hidrógeno atómico con la fuente y el sustrato a altas temperaturas ($\geq 650°$C) durante su proceso de crecimiento. El análisis EDS realizado en las películas muestra también que las impurezas que presentan algunas películas son Si, O y C. Por un experimento adicional se prueba que el origen de los contaminantes Si y O es el efecto que presenta el hidrógeno atómico de atacar al separador de cuarzo y se infiere que la presencia del contaminante C se debe principalmente a la contaminación existente en el reactor.

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*On postdoctoral position.

1. Introduction

Since Nicoll [1] and Robinson [2] developed the close-spaced vapor transport technique (CSVT), it has been successfully used to grow a variety of semiconductor films [3]. This is an efficient and cost effective technique, that allows homo- and heteroepitaxial growth of GaAs layers [4–6]. It consists on a sandwich assembly of a solid source and a substrate separated from each other by a spacer usually of about 1 mm thickness. A temperature gradient is maintained between them, and a transporting agent reacts with the source producing volatile compounds which migrate to the substrate where an inverse reaction takes place forming the epitaxial layer [1,2]. The transport medium is usually water; however, during the last few years some researchers have taken advantage of the atomic hydrogen capability to etch GaAs and other compounds. Petit *et al.* [7] based their GaAs surface cleaning procedure on the reaction mechanism of atomic hydrogen on (001) GaAs surfaces. Angus and co-workers [8,9] used atomic hydrogen in a cyclic fashion to etch graphite from diamond-graphite films in their diamond growth process. Finally, after Kobayashi observation [10] of (100) GaAs etching by atomic hydrogen and its deposition on adjacent substrates, Silva-Andrade and colleagues [11] grew GaAs layers by the CSVT technique using precisely atomic hydrogen as the transport agent. Epilayers obtained by means of this transport agent are open to research since they certainly present many mechanisms that up to now are not well understood for example, the atomic hydrogen incorporation during the growth process and its effect of passivating impurities electrically active, among others.

In this work we use the scanning electron microscopy SEM and energy dispersive spectroscopy EDS techniques to analyze the influence of 4 CSVT setups and some growth parameters on the morphology and the elemental composition of GaAs homolayers grown by the CSVT technique using atomic hydrogen as an initial reactant.

2. Experimental CSVT setups

In this section a short description of the four CSVT setups used in this experiment is given. In setup **a**, Fig. 1, source and substrate are separated by a quartz o'ring spacer. Element 1 is a Sylvania tungsten (W) filament, type EGE, 500 W, 120 V and its temperature is estimated by its change in resistance. This filament generates the atomic hydrogen and contributes to formation of the temperature gradient between source and substrate during the growth process. The molecular hydrogen is carried out into the reaction chamber through the inlet indicated in the figure. The element $1'$ is an uncapsuled Sylvania W filament, type ESY, 150 W, and 120 V, and it also influences the source-substrate temperature gradient.

Setup **b** is very similar to **a** except that the filament $1'$ is of 300 W, 120 V left originally capsuled. In these setups, by fixing the temperature of filament 1, the source temperature was measured as the molecular hydrogen flux was increased, see Fig. 2. Thus, to select a source-substrate temperature gradient one has to take into account the influence of the filaments 1, $1'$ temperature, the spacer thickness, and the molecular hydrogen flux.

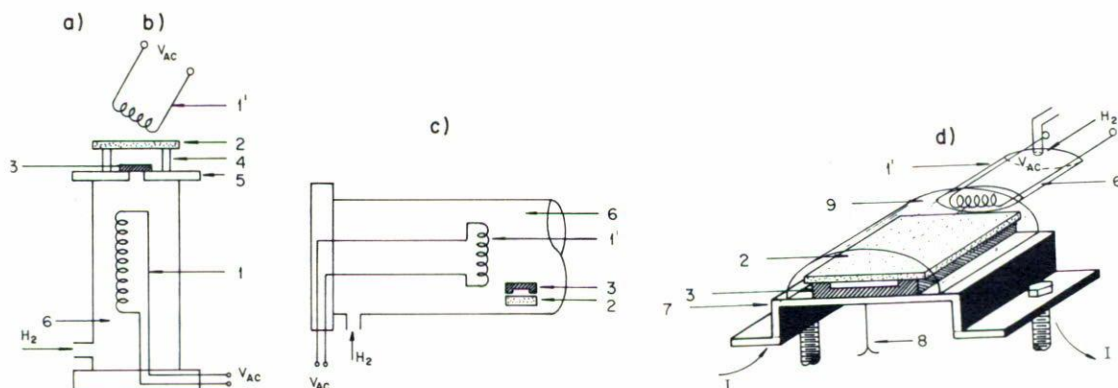


FIGURE 1. CSVT setups, using atomic hydrogen as transport agent to grow GaAs layers. 1. and 1′ are W-filaments, 2. GaAs-Cr doped substrate, 3. GaAs source, 4. quartz o'ring spacer, 5. quartz base, 6. quartz tube, 7. graphite heater 8. k-type thermocouple 9. quartz vault. In setup **d**, I stands for electrical current. The experimental setup **b** is identical to **a** except that the filament 1′ is capsuled.

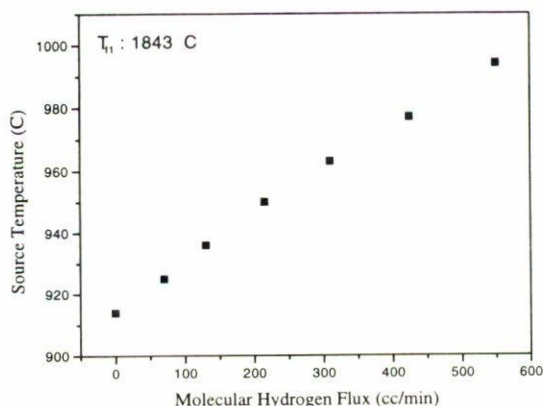


FIGURE 2. Variation of the source temperature in setup **b**, by fixing the filament 1 temperature at 1843°C and increasing the hydrogen flux.

In the setup **c**, Fig. 1, the sandwich source-substrate is positioned 5 mm away from the W filament 1. Previously by photolithography and chemical means a concentric square of about 0.03 mm depth was etch from the source in such a way that, the peripheral step is the source-substrate spacer. This close spacing is to increase the deposition efficiency (gain in weight of substrate/loss in weight of source [4]); unfortunately, this setup does not allow direct temperature measurements of source and substrate. In the setup **d**, Fig. 1, source and substrate are overlapped as in the latter case, the atomic hydrogen generated by the W filament 1′ is led by the quartz vault (9) to pass over the source and substrate, and an additional wafer is put on the substrate backside to avoid its etching. Here heating is caused by Joule effect in the DFP-3.2 Poco Graphite heater, and the source and substrate temperatures were controlled by means of an Eurotherm Mod. 94 temperature controller and a K-type thermocouple.

FIGURE 3. A SEM planar view of the homoepitaxial GaAs layer grown with the experimental setup **a**.

3. Sample preparation

In this experiment undoped (100) $\pm 2^\circ$ (110) GaAs with $n = 10^{16}$ cm^{-3} was used as source and Cr-doped semi-insulating GaAs wafers with (100) $\pm 2^\circ$ (110) orientation, $\rho = 10^8\ \Omega \cdot$cm and EPD = 5–7 $\times 10^4$ cm^{-2} as substrates. The wafers were first degreased by the ultrasonic cleaning in acetone, xylene, acetone, and rinsed in deionized (DI) water. The clean wafers were then etched in 3:1:1 (H_2SO_4:H_2O:H_2O_2) etchant at $T = 80^\circ$C, then each sample was dipped into 1:1 (HCl:H_2O) solution, to remove residual surface oxides just prior introduction into the reaction chamber [12]. Finally, the sample was rinsed in DI water and dried by a spinner.

4. Results and discussion

The surface morphology and stoichiometry of the "as grown" GaAs layers were analyzed using a JSM-5400LV (JEOL) scanning electron microscope (SEM) in combination with a (Voyager Noran) energy dispersive X-ray spectrometer.

Figure 3 presents a plan view SEM micrograph of the GaAs layer grown by the CSVT setup **a** with a spacer of 2 mm thickness. In this figure a kind of polycrystalline structure is observed, according to Sheldon [13] it corresponds to a three-dimensional growth. This structure is uniform in the central area of the grown layer while, in the periphery close to the delimiting o'ring spacer some density of pit defects (DPD) appears. The characteristic morphology of the layer grown with the setup **b** also with a spacer of 2 mm thickness, is shown in Fig. 4a, as can be observed, it is smooth and uniform, but similarly to the former layer, presents pit defects (PD) on its outermost peripheral area, whose density varies from 1.8×10^4 to 7×10^5 cm^{-2}; Fig. 4b shows a SEM magnified image of some pit defects for their better visualization. We infer that these PD are similar to the ones reported by Guelton *et al.* [6] which, in their study of GaAs films grown by CSVT using water as the transport agent, were analyzed with optical microscopy or, to the ones reported by Uen *et al.* [14] that were analyzed with SEM at low magnification and classified as threading dislocations.

As shown in Table I, these two layers were grown with identical parameters, except for the substrate temperature, which causes different source-substrate temperature gradients

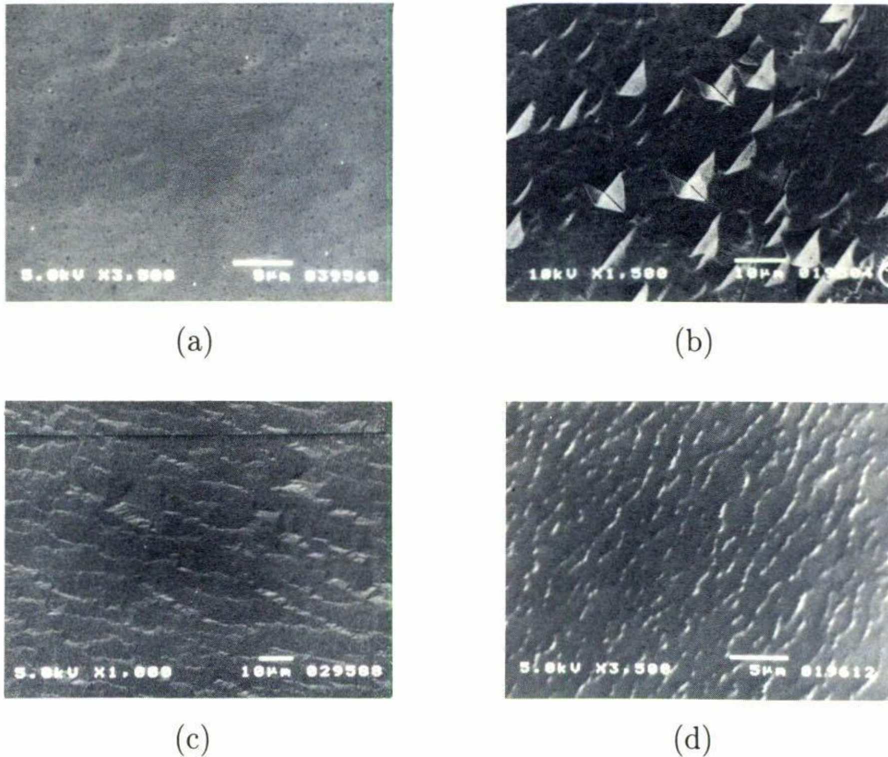


FIGURE 4. Characteristic surface morphology of the homoepitaxial GaAs layers deposited with the experimental setup **b**. (a) and (b) of the sample grown using a spacer of 2 mm thickness, (c) and (d) of layers grown with a spacer of 1 mm thickness at different source-substrate temperature gradients.

during the growth processes. Then, the difference in morphology is attributed to the difference in gradient temperature, thus the greater the temperature gradient the less homogeneous the film is.

Other GaAs layer was grown with setup **b**. For this deposition the thickness spacer $\delta = 1$ mm and a molecular hydrogen flux of 425 cm^3/min were used. With these parameters values, the source-substrate temperature gradient is a slightly less than the one of the former growth. However the surface morphology of this layer shown in Fig. 4c, shows a kind of "terraces". This type of morphology has been already reported in other studies [17, 18], and it is a subject of much research nowadays due to its possible use in quantum effect devices.

A considerable change in surface morphology with respect to the former sample is observed when keeping the former values for the molecular hydrogen flux and spacer thickness, the filaments temperatures and consequently the source-substrate temperature gradient are decreased. The morphology has an orange peel appearance as shown in the SEM micrograph, Fig. 4d. This layer and the former do not contain pits but oval defects [15], whose densities are much less than the DPD of layer 6.9. The GaAs layers grown with setup **c** show slightly different surface morphologies, see Figs. 5a and 5b,

TABLE I. CSVT experimental setups and parameters used to grow GaAs homoepitaxial layers.

Setup	Sample No.	H_2 flux cm^3/min	Spacer thickness mm	Filament 1 temp. °C	Source temp. °C	Substrate temp. °C	ΔT °C
a	6.5	310	2	1843	963	662	301
b	6.9	310	2	1843	963	736	227
b	HT4	425	1	1843	975	760	215
b	HT1	425	1	1724	850	700	150
c	7.8	425	0.03	1640	—	—	—
c	8.3	425	0.03	1490	—	—	—
d	7.2	425	0.03	1840	825	800	25

(a)

(b)

FIGURE 5. SEM images of GaAs layers grown with the experimental setup **c**. The filament temperatures were: (a) 1640°C and (b) 1490°C.

probably due to the different temperatures of filament 1 used during their grow processes. Although the small difference in texture both morphologies can be classified as orange peel type.

Figure 6 shows the surface morphology a GaAs layer grown with setup **d**. It is a kind of fine nucleation, it looks like an orange peel texture in formation however, it is hard to say that with further growth it will resemble the orange peel morphology of the samples above. Let us mention that, the orange peel appearance of the GaAs layers has been already reported [19, 20] but a direct comparison to those studies was not possible.

By the above analysis, let us note that, one parameter of great influence on the surface morphology of the GaAs layers is source-substrate temperature gradient. We observe that, the "best" surface morphologies were obtained with setup **b**, at the smaller source-substrate temperature gradients, in the sense that they are homogeneous throughout the growth area and present less defect densities.

Furthermore, an EDS analysis of many areas of the GaAs layers and their defects was done. A detailed study of the defects found in this set of layers is given elsewhere [16].

TABLE II. EDS atomic percentages of Ga and As of the GaAs layers grown with different CSVT setups and atomic hydrogen as initial reactant.

	Element	
	Ga	As
Sample	Atomic %	
6.5	52.99	47.01
6.9	52.59	47.41
HT4	52.28	47.72
HT1	52.20	47.80
7.8	53.17	46.83
8.3	52.96	47.04
7.2	53.26	46.74

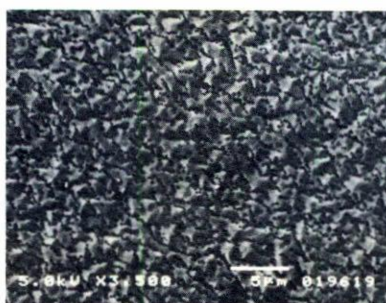


FIGURE 6. Scanning electron microscope picture of the GaAs layer grown with the experimental setup **d**.

Table II summarizes the atomic percentages of the elements constituting the layers, these data are representative of areas whose morphology is characteristic of the sample under study. It is observed from this table that all GaAs layers under study present a stoichiometric deviation in their elemental composition, Fig. 7 shows an EDS spectrum taken from the center of sample 6.9.

In addition to Ga and As, signals of considerable intensity corresponding to Si, O, and C appear in the EDS spectra of some samples. In regard to Si and O contaminants, the authors of this work inferred that their incorporation was due to the quartz o'ring spacer etching by atomic hydrogen specially, because their signals are null in layers grown with setups with no quartz spacer. A common fact is that their signals are more intense on external than on internal areas close to the spacer and negligible on the area beneath it. An additional experiment confirmed this supposition. It basically consisted on replacing the GaAs source by a quartz plate in setup **b** and running the deposition procedure for 30 min. Figure 8 shows 2 EDS spectra: (a) the spectrum taken at the edge of the GaAs

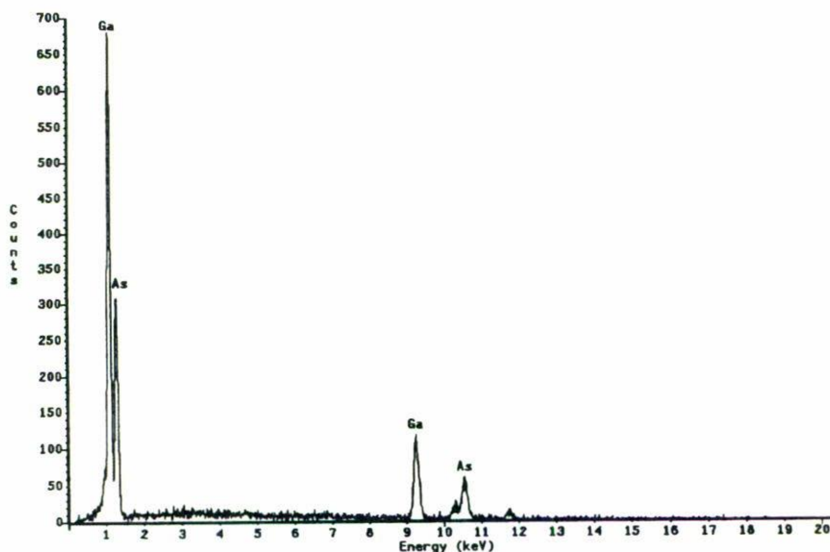


FIGURE 7. Shows an EDS spectrum corresponding to the GaAs layer, sample 6.9.

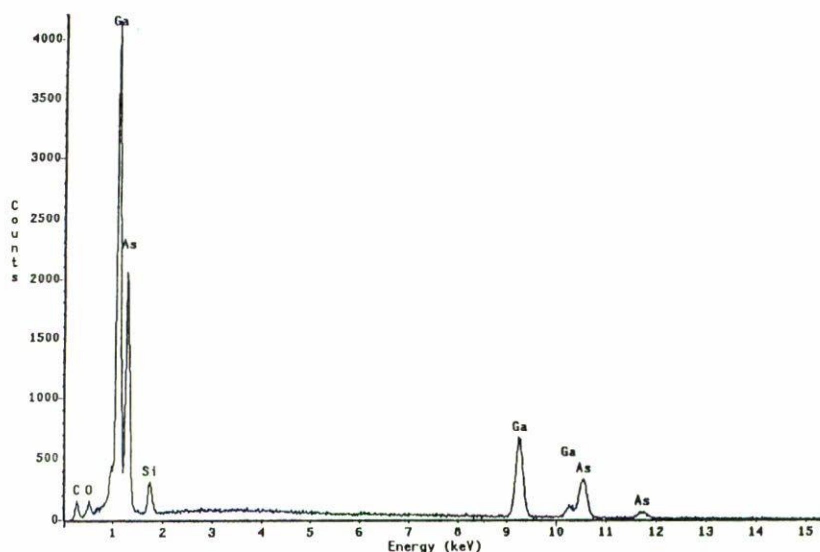
layer (6.9), and (b) the spectrum of the layer grown with the quartz plate as source. Thus these spectra prove that the atomic hydrogen presents the same etching effect for SiO_2 as for GaAs. (This effect was not found in the literature.) Concerning the C signal, its possible origin is contamination in the reactor, since it is not a high vacuum system besides, by a similar fashion to the former contaminants, graphite etching by atomic hydrogen [8, 9] from the graphite heater in the setup **d**.

The stoichiometric deviation presented by all GaAs layers under study is more likely produced by the use of atomic hydrogen at high substrate temperatures ($\geq 650°$C) during their growth processes, since according to Sugata *et al.* [21] interaction of atomic hydrogen at a GaAs temperature less than 400°C leaves the Ga and As stoichiometry unchanged; thus, for the meantime the reaction mechanism etching-growth of GaAs by atomic hydrogen is not well understood. Further studies about this subject are in progress to improve the quality of the layers, determine their crystallinity, and elucidate the growth mechanism.

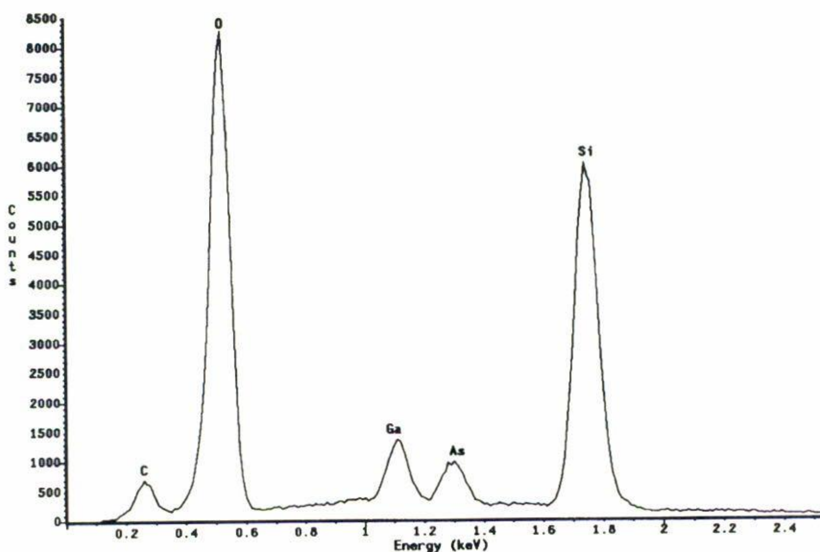
5. CONCLUSIONS

It has been observed in this study that the surface morphology of the GaAs layers grown by the CSVT technique using atomic hydrogen as initial reactant is dependent of the source-substrate temperature gradient. To this temperature gradient contribute: the temperature of the filaments 1 and $1'$, the spacer thickness, and the molecular hydrogen flux in the setups **a** and **b**.

From the morphological analysis by SEM we conclude that the GaAs layers with the "best" morphologies were grown with the setup **b** at the smaller source-substrate



(a)



(b)

FIGURE 8. Shows EDS spectra: (a) Taken at the edge of the GaAs layer, sample 6.9, and (b) Taken from the layer, whose deposition was done having a SiO_2 plate as source.

temperature gradients, since they are homogeneous throughout the growth area and present less defect densities.

From the EDS analysis it is observed that all GaAs layers reported here showed a stoichiometric deviation that is, the surface is rich in Ga, due to a noncoherent close

spaced reaction during the growth processes. Furthermore, by an additional experiment it was proved that the Si and O contamination found on some layers was due to the etching effect of the quartz spacer by the atomic hydrogen, and it is inferred that the C contamination is mainly due to some contamination existing in the CSVT reactor.

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