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Rapid Thermal Annealing Treatment of Electroplated Cu Films

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Cu seed layers for copper electroplating were deposited by magnetron sputtering on silicon wafers using TaN as diffusion barriers between the seed layer and silicon. The Cu seed layer was cleaned with a H_2 plasma prior to electroplating the copper film, and the effects of the H_2 plasma pretreatment were investigated. After thin copper films were grown by electrodeposition on the copper seed layers which had been cleaned with the H_2 plasma, they were then subjected to i) vacuum annealing, ii) rapid thermal annealing (RTA) and iii) rapid thermal nitriding (RTN) at various temperatures over different periods of time. X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and resistivity measurements were done to ascertain the optimum heat treatment conditions for obtaining films with minimum resistivity and with smooth, predominantly (111)-oriented surfaces. The as-deposited film had a resistivity of ∼6.3 $\mu\Omega$-cm and a relatively small intensity ratio of the (111) to the (200) peak. With heat treatment, the resistivity decreased and the (111) peak became dominant. In addition, the surface smoothness of the copper film was improved. The optimal condition (with a resistivity of 1.98 $\mu\Omega$-cm) is suggested to be rapid thermal nitriding at 400 °C.

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I. INTRODUCTION

In ultra-large integrated circuit (ULSI) fabrication, copper is widely accepted as a new interconnect material to replace aluminum and its alloys due to its low resistivity (∼1.7 $\mu\Omega$-cm) and high electromigration resistance [1–4]. Cu films can be obtained by several different deposition techniques, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and plating such as electroless plating and electroplating. Especially, electroplating is a very inexpensive process in principle and offers a high deposition rate, so that many research groups have successfully used it to fill via holes and trenches with high aspect ratios in dual damascene structures [5,6]. Therefore, today, copper electroplating is widely accepted as the most popular technique to fill trenchs or vias [5].

A conformal and conductive seed layer is necessary for copper electroplating [6]. The seed layer provides a low resistance path for the plating current in the electrodepoition process and facilitates nucleation of the plated copper film. In addition, the seed layer should have low levels of impurities, a smooth interface, good adhesion to the barrier metal, a low thickness, and coherence to ensure a void-free fill [7]. The electrical conductivity of the surface plays an important role in the formation of the initial Cu nuclei. The nucleation processes of copper are also well known to be very sensitive to the surface conditions [8].

The seed layers deposited by sputtering may contain some impurities like F, O, C, N, S, Cl, *etc.* The removal of these contaminants is essential for proper electrodeposition of copper. Plasma cleaning, employing hydrogen as a reactive gas, has been recognized as a wafer-cleaning technique. The reason behind the utilization of a H_2 plasma is that most of the contaminants form volatile hydrides during the process and can be removed from the cleaning chamber easily [9].

In the present communication, we focus on different post deposition heat treatments to find out how they affect the properties of the copper films deposited on H_2-plasma-cleaned copper seed layers. Previous studies on Cu films reported growth with (111), (200), and random texture components [9,10], of which the (111) orientation afforded better electromigration performance [11]. Thus, heat treatment of the as-deposited Cu film may result in reorientation of the crystal structure in the desired (111) direction. The purpose of the present work is to obtain copper films with a) minimum resistivity, b) a texture

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predominately oriented in the (111) direction, and c) a smoother surface morphology.

II. EXPERIMENT

Copper seed layers (500 Å) were deposited onto tantalum nitride barrier layers by using magnetron sputtering with a Cu target in an Ar gas atmosphere before electroplating of copper in the forward pulsed mode. Prior to electroplating the copper film, the Cu seed layer surface was cleaned with hydrogen-plasma treatment. A sputtered 500-Å-thick TaN film was used as diffusion barrier and adhesion promoter. The Cu seed/tantalum nitride/silicon samples were rinsed with deionized (DI) water for 3 min, followed by filtered nitrogen drying, before the hydrogen-plasma treatment. The plasma treatment was conducted in a parallel-type cold-wall reactor of a plasma-enhanced-chemical-vapor deposition (PECVD) system that had been pumped down to a base pressure of 10^{-6} Torr. The plasma exposure time during the plasma treatment was varied from 1 to 20 min, and the rf-power was varied from 20 to 140 W while keeping the flow rate of hydrogen and the substrate temperature constant at 100 sccm and 25 °C, respectively. After the H_2-plasma treatment, copper electroplating was conducted on each substrate.

The electroplating system mainly consists of a copper plating solution (a sulfuric acid- copper sulfate chemical solution without organic additives), a soluble anode, a wafer (which serves as a cathode), and a duty power supply. A forward pulsed current was used for electroplating because it improved the via trench filling capability. Then, copper in the copper plating solution was electroplated onto the plating substrate metal surface, which acted as the negative electrode of the electrochemical cell. The copper-plating current density was kept fixed at 60 mA/cm^2.

The electroplated copper films were annealed by using various processes, such as vacuum furnace annealing for 5 min, rapid thermal annealing (RTA) for 15 sec and rapid thermal annealing (RTN) in a pure N_2 environment for 15 sec, at various temperatures ranging from 200 °C to 500 °C. The surface morphology of the Cu seed layers and the effects of annealing on the copper films electrodeposited on the H_2-plasma-cleaned copper seed layer were investigated. The electroplated films were characterized using atomic force microscopy (AFM) (Topomatrix Corporation: Accurex II) and scanning electron microscopy (SEM) (Hitachi S-4200). The resistivities of the electroplated copper films were measured by using a four-point probe. The levels of impurities and the surface chemical bonding states of the Cu seed layers were investigated by using X-ray photoelectron spectroscopy (XPS) (VG SCIENTIFIC, ESCALAB 220i-XL). The crystallographic orientation of the Cu films was investigated by using X-ray diffraction (XRD, Philips X'pert MPD).

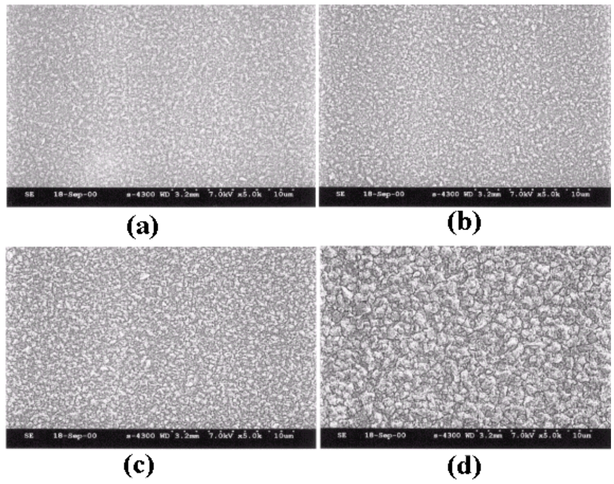

Fig. 1. SEM micrographs (×5000) of the electroplated copper films after the plasma pretreatment of the Cu seed layer at various rf-powers (exposure time: 10 min.): (a) 20 W, (b) 60 W, (c) 100 W and (d) 140 W.

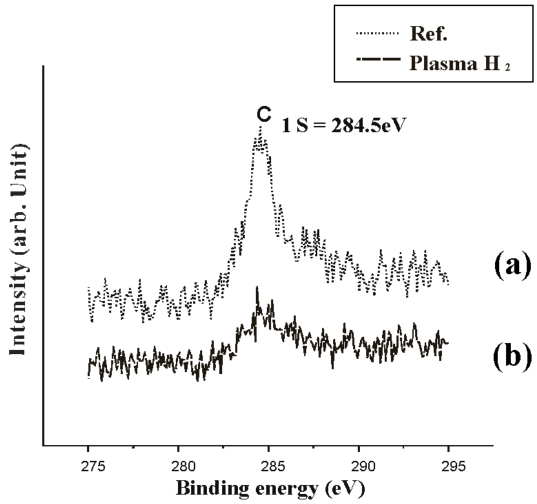

Fig. 2. The XPS C1$_S$ peak (284.5 eV) of the Cu seed: (a) reference (b) H_2 plasma pretreatment (100 W, 10 min.) of the Cu seed layer.

III. RESULTS AND DISCUSSION

We have studied the effects of H_2-plasma pretreatment and the combined effects of H_2-plasma pretreatment and rapid thermal annealing of Cu seed layers on the surface morphology and the resistivity of electroplated copper films. The SEM micrographs of the electroplated copper films with H_2-plasma pretreatments of the Cu seed layers at various rf-powers for a constant exposure time of 10 min prior to the electroplating are shown in Fig. 1. The figure indicates that the grain sizes of the copper films are nearly the same, but for the sample pretreated with an rf-power of 140 W, the grain sizes were relatively large.

The improvement in the surface roughness of the electroplated samples after H_2-plasma pretreatment of the

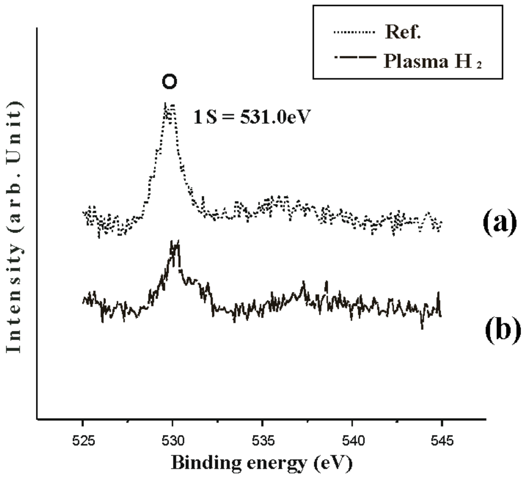

Fig. 3. The XPS $O1_S$ peak (531.0 eV) of the Cu seed: (a) reference (b) plasma hydrogen pretreatment (100 W, 10 min.) of the Cu seed layer.

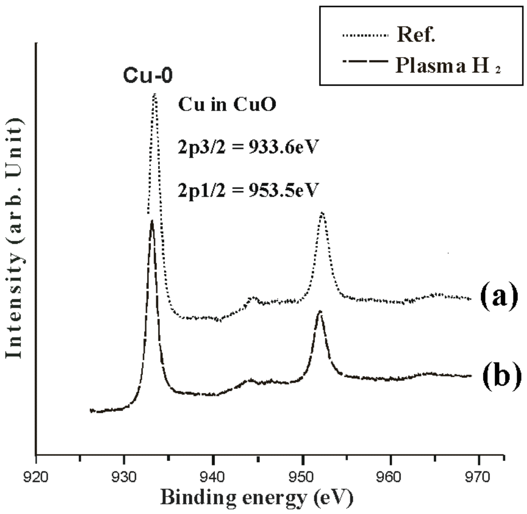

Fig. 4. The XPS $Cu2_P$ peaks of the Cu seed: (a) reference (b) plasma hydrogen pretreatment (100 W, 10 min.) of the Cu seed layer.

Cu seed layer can be interpreted in terms of the cleaning ability of the H_2 plasma. There are various kinds of impurities, such as F, O, C, N, Cl, *etc.*, present in the Cu seed layer. The $C1_S$ peak (284.5 eV) and the O1s peak (531.0 eV) in the XPS spectra of the Cu seed layer are shown in Figs. 2 and 3, respectively, and indicate that the top of the seed layer contains carbon and oxygen impurities. Cu (in CuO) $2p_{3/2}$ and Cu (in CuO) $2p_{1/2}$ peaks were also observed at 933.6 eV and 953.5 eV, respectively (Fig. 4). The effects of the H_2-plasma pretreatment are also presented in Figs. 2, 3, and 4, which show that the heights of the C, O, and CuO peaks of the Cu seed layer are decreased by the H_2-plasma pretreatment. Enrichment of oxygen and carbon at the interface of the electroplated copper film and the Cu seed layer

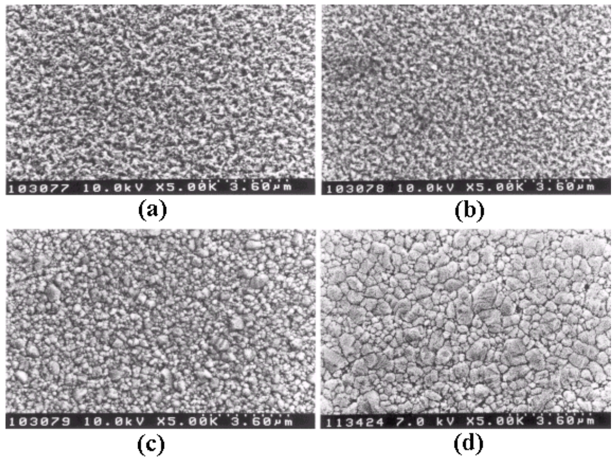

Fig. 5. Scanning electron micrographs of the copper films after vacuum furnace annealing for 5 minutes at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

can be the cause of poor wetting and peeling of the electroplated copper film, and hence the roughness of the film.

The chemistry of the removal of these contaminants was explained by Korner *et al.* [9]. They showed that the main byproducts of H_2-plasma cleaning of C and O contaminations were CH_4 and H_2O. During H_2-plasma cleaning, hydrogen atoms react with oxygen and carbon atoms to form H_2O and CH_4, respectively, as follows:

$$CuO + H_2 \rightarrow Cu + H_2O \quad (1)$$

$$C + H_2 \rightarrow CH_4 \quad (2)$$

The volatile H_2O and CH_4 can be easily evacuated from the plasma chamber. Hence, after the H_2-plasma treatment, the seed layer surface contains more free Cu atoms, which may enhance copper nucleation during copper electroplating.

Figure 5 shows scanning electron micrographs of the grown copper film after vacuum furnace annealing at various temperatures up to 500 °C. The as-deposited film consists of small spheroidal grains with randomly curved grain boundaries. The grains grow considerably in size, with increasing annealing temperature [12]. The coexistence of large and small grains (twin formations) indicates secondary grain growth has occurred. Like Harper *et al.* [13], we also note that the appearances of the grains that have not grown in size are different from those of the grains of the as-deposited sample. As a result of annealing beyond 400 °C, the copper film seems to have undergone a complete recrystallization. Since the intersection of the twin boundaries depends on the orientation of the grains [14], we find that more than one crystal phase may be present in the film. The relative ratio of the phase was determined by using XRD and is reported later.

Figures 6 and 7 exhibit the SEM micrographs of copper films treated with rapid thermal annealing (RTA) and

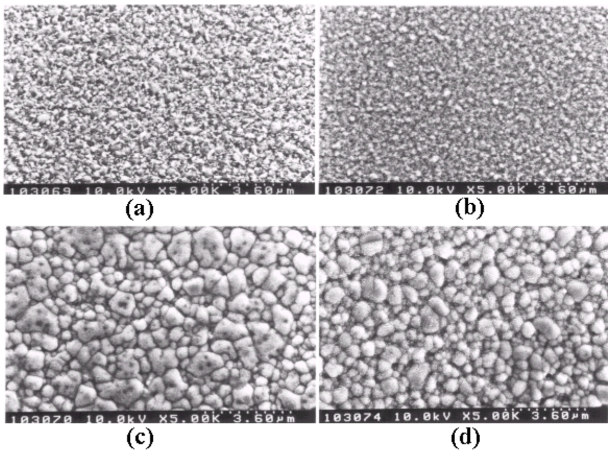

Fig. 6. Scanning electron micrographs of the copper films after rapid thermal annealing (RTA) for 15 sec at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

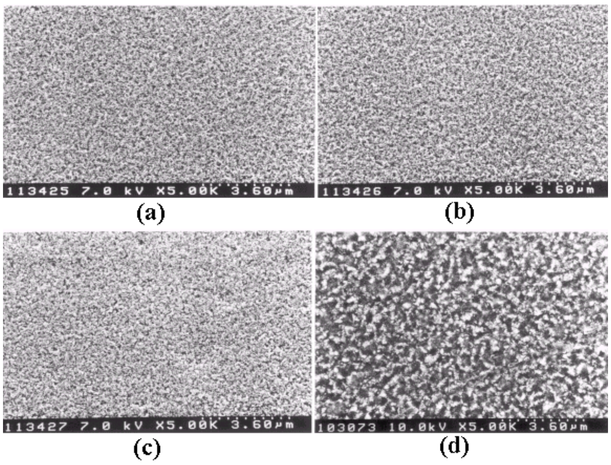

Fig. 7. Scanning electron micrographs of the copper films after rapid thermal nitriding for 15 sec at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

rapid thermal nitriding (RTN), respectively, at different temperatures. It is noted from these figures that the growth of grains is more dominant in the case of RTA than RTN. In fact, in the case of RTN, the grains remain similar until 400 °C, after which the grains are slightly restructured.

Figures 8, 9, and 10 show the X-ray diffraction patterns of the different heat-treated films. From these figures, we find that the as-deposited films consist of two types of textures, viz. Cu (111) and Cu (200). With increasing treatment temperature, the relative intensity ratio of the (111) peak to the (200) peak increase for all types of heat treatment. Thus, during the crystallization, due to heat treatment the grains become more oriented in the (111) plane [15]. Although the mechanism of recrystallization may differ for different types of thermal treatment, the grains can be seen to tend to

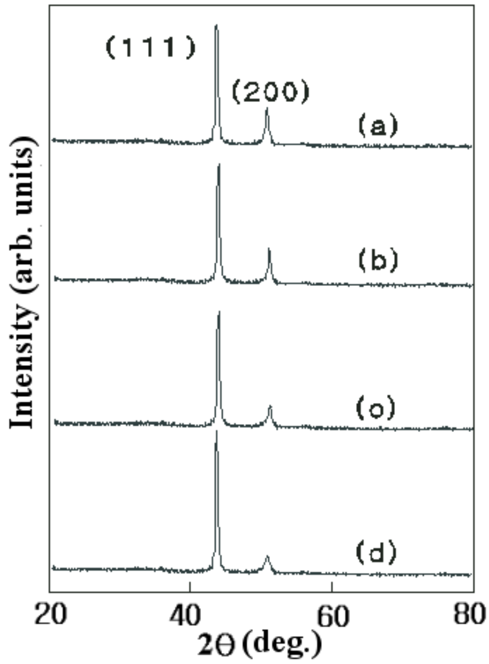

Fig. 8. X-ray diffraction patterns of the copper films after vacuum furnace annealing for 5 minutes at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

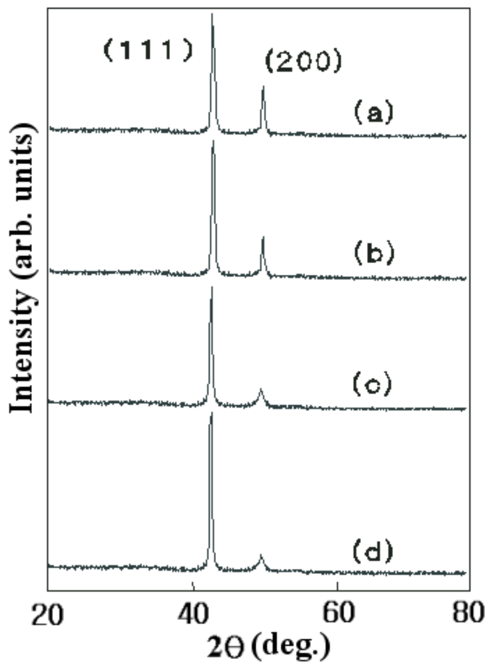

Fig. 9. X-ray diffraction patterns of the copper films after rapid thermal annealing (RTA) for 15 sec at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

orient in the (111) direction for all cases.

Figure 11 shows the electrical resistivity *vs.* temperature plots for different types of post-deposition heat

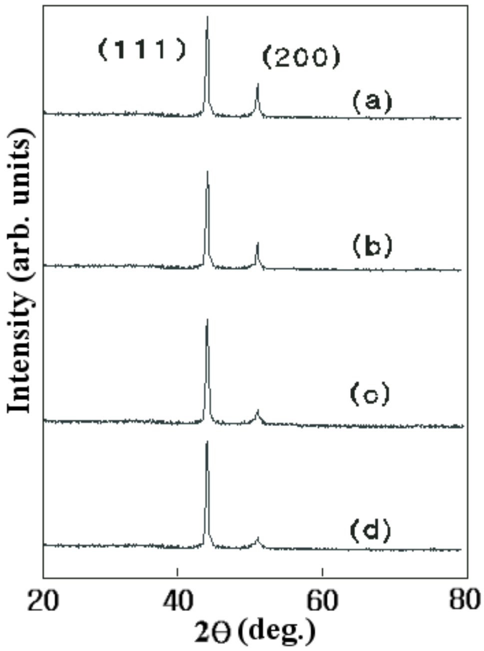

Fig. 10. X-ray diffraction patterns of the copper films after rapid thermal nitriding for 15 sec at different temperature (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

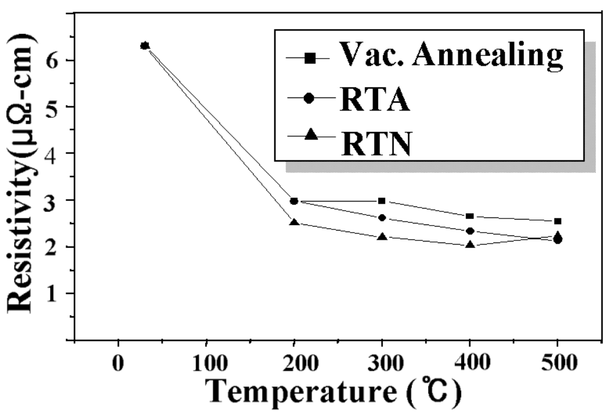

Fig. 11. Electrical resistivity *vs.* temperature plots for different types of heat treatment.

treatments. We find that the resistivity decreases with increasing treatment temperatures in all the cases. From SEM micrographs and the resistivity plots, we can correlate the drop in resistivity with the grain growth. Park *et al.* [16] proposed that the reduction in electron scattering at the grain boundaries was linked to secondary grain growth of electroplated Cu films. From our heat-treated specimens, we can confirm the secondary grain growth. This in turn reduces the electron scattering, which results in low resistivity and better electromigration. Thus, our results support the model proposed by Park *et al.* [16].

In our case, the different as-deposited films have a resistvity of 6.3 $\mu\Omega$-cm. After various heat treatments, the lowest resistivity found was for rapid thermal nitriding (RTN) done at 400 °C, in which case the resistvity is reduced to 2.03 $\mu\Omega$-cm. The reason why the resistivity of the RTN-annealed Cu film is lower than that of the RTA or furnace annealed (FA) Cu film may be that the native oxide is more difficult to form on the former than on the latter. Since the strength of the Cu-N bond is larger than that of the Cu-O bond, once the Cu atom bonds with a nitrogen atom, that bond cannot be broken for the Cu atom to form a new bond with an oxygen atom. The resistivity of Cu or CuN is well known to be lower than that of CuO or Cu_2O. Therefore, the RTN-annealed Cu film has a lower resistivity than RTA or FA-Cu film. From the above experimental results and discussion, we find that the best tradeoff condition to obtain copper films with minimum resistvity, small crystallites (or, as a consequence, low surface roughness) and the highest degree of (111) preferred orientation is rapid thermal nitriding (RTN) at 400 °C.

IV. CONCLUSIONS

H_2-plasma pretreatment of Cu seed/tantalum nitride/silicon samples can improve the surface conditions for electroplating of copper because this treatment can remove carbon and oxygen contaminants from the seed layer, allowing more copper atoms to be free for electroplating. Heat treatment processes, including vacuum furnace annealing, rapid thermal annealing (RTA) and rapid thermal nitriding (RTN) were used with the sample, and as a general trend, the resistivities of all the samples were found to decrease with increasing treatment temperature. At the same time, the as-deposited copper films with (111) and (200) textures aligned themselves along the predominantly (111) direction after heat treatment. If the results are combined, the best tradeoff for obtaining films with minimum resistivities, smooth surfaces, and high degree of (111) preferred orientation is rapid thermal nitriding (RTN) at 400 °C.

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