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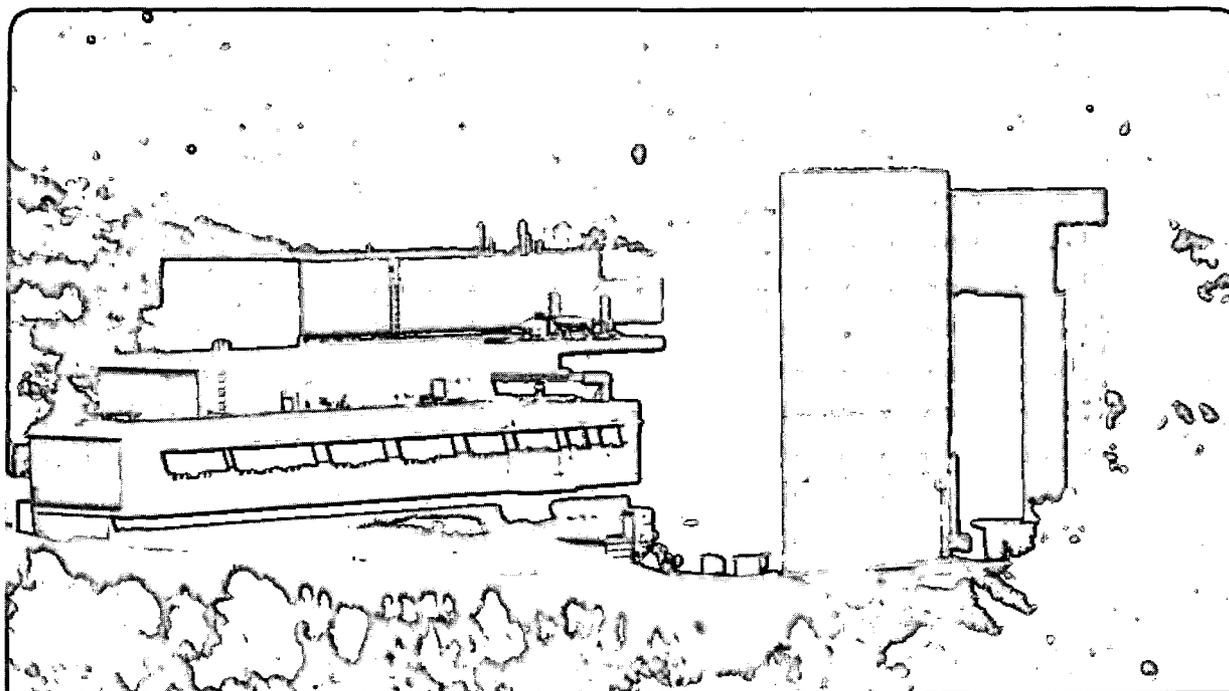
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CONTROL OF TEXTURE DURING VAPOR DEPOSITION OF Al ON (111) Si

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ABSTRACT

The growth of Al on (111) Si single crystal substrates by various techniques usually leads to films with (111) texture, sometimes with a small (100) component. Using X-ray diffraction and electron microscopy, the present study shows that the (100) texture component can be enhanced to the point of forming an oriented (100) continuous tricrystal structure. The formation of this texture is shown to be related the presence of Cu. It is concluded that an understanding of heteroepitaxy must take into account the effect of chemistry in addition to the crystallographic criteria of lattice matching.

INTRODUCTION

Heteroepitaxial deposition of Al on Si has been studied by a number of investigators [1]. For (111) Si substrates it is generally found that Al grows with (111) texture, often with parallel epitaxy, i.e. in a cube-cube orientation relationship. The best-quality films have been grown by the ionized cluster beam technique [2], but even vapor deposition leads to near-single crystal films of (111) Al in parallel epitaxy [3]. These data alone might lead to the conclusion that parallel epitaxy would always be expected between Si and Al. However, Al grown on (001) Si substrates shows a quite different (110) alignment that results in a continuous bicrystal arrangement with unique and interesting properties [4]. It was also reported that vapor deposition on (111) substrates led to a small component of (100) texture in addition to the major component of (111)-oriented Al [3]. The present work was undertaken in an effort to understand the factors that control the film quality and orientation relationship in heteroepitaxial growth.

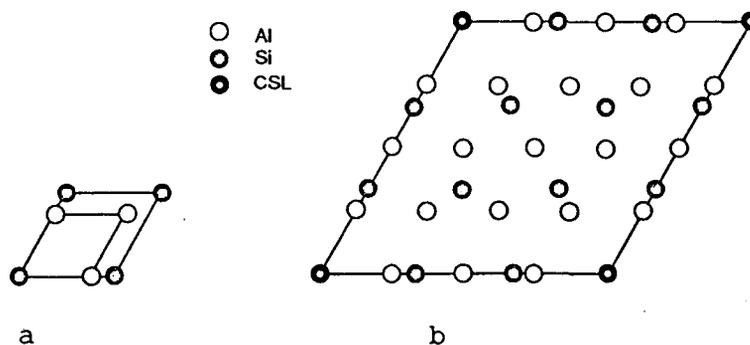


Fig. 1 Superimposed (111) planes of Si and Al at 280°C where the direct mismatch between the lattices is 25% (a) but a perfect coincidence exists between every 3 Si spacings and every 4 Al spacings (b). The perfect match would be expected to lead to the parallel epitaxy illustrated here.

Geometric models based on the near-coincidence-site lattice (near-CSL) concept [5] have been used with some success as criteria for heteroepitaxial growth [6,7]. For parallel epitaxy of Al on Si the direct mismatch between the two lattices is 25%, see fig. 1a. However, the near-CSL criterion shows that 3 unit cells in Si are very nearly equal to 4 unit cells in Al. In this comparison there remains only a 0.6% mismatch. Due to the different thermal expansion

coefficients of Al and Si, this mismatch becomes even smaller at elevated temperature. Using the available data on thermal expansion coefficients for Al and Si [8] it was calculated that a perfect 3:4 match between Si and Al is expected at 250 - 280°C. A schematic illustrating the perfect near-coincidence site lattice match at this temperature is shown in Fig. 1b. The matching 2-dimensional supercell in the (111) interface plane is outlined. Note, however, that only 4 out of 16 Al and 9 Si lattice sites in the interface are in coincidence site positions.

EXPERIMENTAL

Substrate single crystal p-type (111) wafers with 3" diameter and a resistivity of 7-21 Ωcm were cleaned by the following procedure: Initially, the substrates were oxidized for about 10 min in a solution of 1:1 by volume hydrogen peroxide and sulfuric acid, cleaned with deionized water, etched for about 10 min. in a solution of 10% HF in deionized water, followed by a water rinse. Immediately after cleaning the wafers were loaded into a vacuum chamber with a base pressure of 2×10^{-7} mbar. The wafer could be heated to 500°C via a substrate heater with a Cu base. Films of 100-300 nm thickness were deposited from an Al charge of 99.999% purity onto the cleaned Si substrates held at various temperatures between room temperature and 450°C. The as-deposited films were characterized by X-ray diffraction, SIMS and transmission electron microscopy. Plan view TEM samples were prepared by cutting 3mm discs, dimpling from the substrate side to less than 10 μm and Ar ion thinning to electron transparency. Cross section samples were prepared by the method described by Bravman and Sinclair [9].

RESULTS

Initially a series of depositions was performed at different substrate temperatures. The resulting films were characterized by X-ray diffraction and the degree of texture was determined by converting peak intensities to volume fractions. The results are shown in the form of a bar graph in fig. 2. At room temperature, a strong (111) texture with random in-plane orientation was observed. As the temperature was increased, a small fraction of (100)-oriented grains appeared and its volume fraction increased with temperature. This steady increase could indicate either an increased lattice mismatch or a thermally activated process such as impurity diffusion. As shown above the lattice match criterion would predict an optimum at $\sim 280^\circ\text{C}$, in contradiction with the observed behavior.

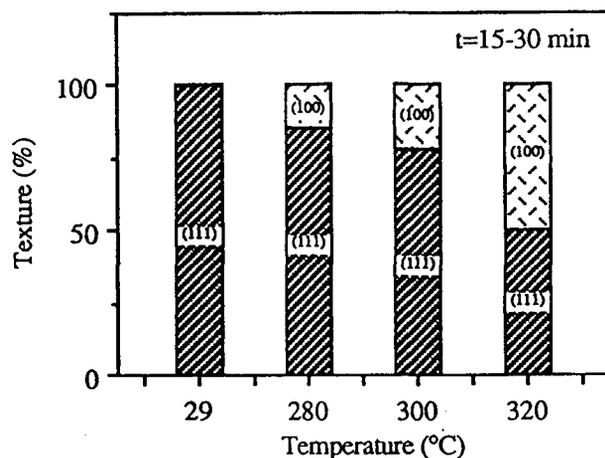


Fig. 2 Bar graph showing increasing fraction of (100) texture with increasing substrate temperature. Data summarized from X-ray diffraction measurements.

If impurity diffusion was involved, a dependence on holding time at temperature before the start of the deposition process would be expected. Fig. 3 shows the result of a comparative set of depositions performed at the same temperature with and without prior isothermal holding. It is clearly apparent that the fraction of (100) texture increases dramatically if the substrate is held for 3h at temperature before deposition.

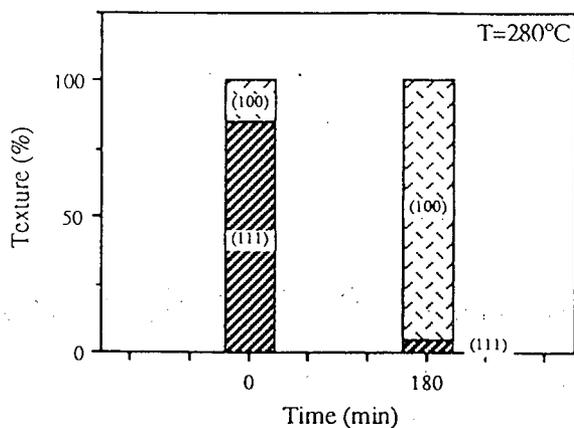


Fig. 3 Bar graph illustrating the effect of isothermal holding time before deposition.

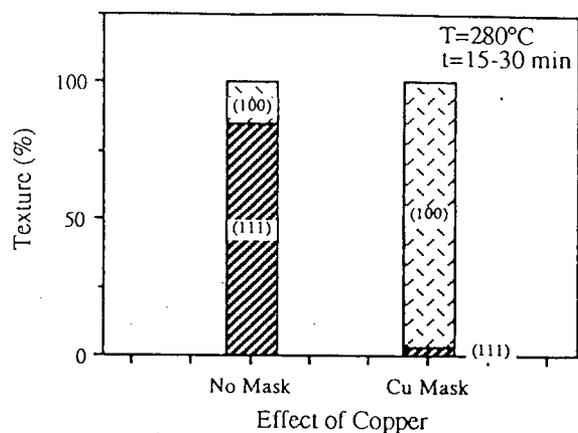


Fig. 4 Bar graph illustrating the effect of Cu on Al texture

For good conductance the substrate heater base was made of Cu which is known to be a fast diffuser in Si with a diffusion coefficient of $5.7 \times 10^{-7} \text{ cm}^2/\text{s}$. It can be calculated that at 280°C , a time of about 1h would be sufficient for the Cu to cross the $500 \mu\text{m}$ thick Si substrate. To detect the presence of Cu in the Al film or at the interface, several films were analyzed by SIMS. However, in most cases, the Cu content was below the detectable limit, even at the interface. Further experiments were therefore performed to confirm the effect and isolate its origin.

Two extreme conditions were employed and the results are shown in fig. 4. When the substrate was in direct contact with Cu by using a Cu hold-down clamp on its top surface, an extreme (100) texture was observed, even if the deposition was started as soon as a stable temperature was reached, i.e. at zero holding time. Comparing this with a film grown at zero holding time (no time for Cu diffusion through substrate) and without a Cu mask on its surface (left bar) illustrates the effect of Cu on the Al texture clearly. Furthermore, when the Si substrate was isolated from contact with the Cu holder by using a Ta sheet as a diffusion barrier, a similar (111) texture was observed, even after a holding time of 4h at 280°C . It was thus concluded that Cu induces the change from a (111) to a (100) texture.

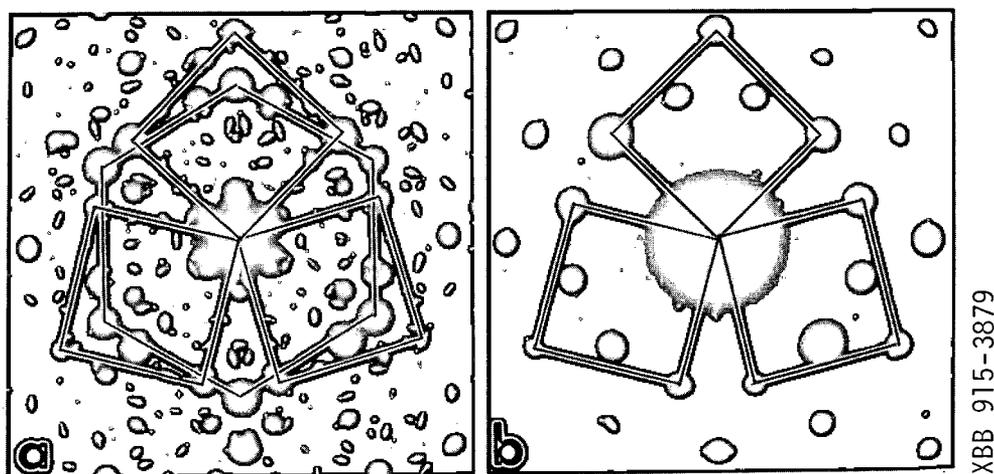


Fig. 5 Selected area diffraction patterns of Al on Si (a) and freestanding Al film (b). In (a) the Si (111) pattern is outlined by a hexagon and the three orientation variants of (100) Al are shown as squares. In (b) the Si substrate was removed and the tricrystal orientation relationship is more apparent.

To complement the X-ray diffraction data which showed a predominant (100) texture, electron diffraction was employed to check for in-plane alignment. Fig. 5a shows a diffraction

pattern obtained from an Al film on its Si substrate. Although a confusing array of diffraction spots is present in this pattern, an epitaxial alignment is apparent.

To simplify the interpretation of this pattern the (111) diffraction pattern of the Si substrate has been outlined by a hexagon and the (100) patterns of the Al are marked by squares. The orientation relationship is one in which close packed $\langle 110 \rangle$ directions in the two crystals are parallel in the interface, while the (100) planes of Al are parallel to the (111) surface of the Si substrate, i.e.

$$(100)_{\text{Al}} \parallel (111)_{\text{Si}} \quad \text{and} \quad [011]_{\text{Al}} \parallel [01\bar{1}]_{\text{Si}}.$$

There are three orientation variants of the (100) Al pattern because there are three equivalent ways of orienting (100) Al on (111) Si in such a way that the close packed directions are aligned. Fig. 5b shows an equivalent pattern in a region where the Si substrate was removed. The sixfold pattern of the Si along with all double diffraction is now missing and it is much easier to recognize the three orientation variants of the Al film which are again outlined by squares. The three patterns are related to each other by 120° rotations. However, because each pattern itself has fourfold (90°) rotational symmetry, this is identical to a 30° misorientation between variants.

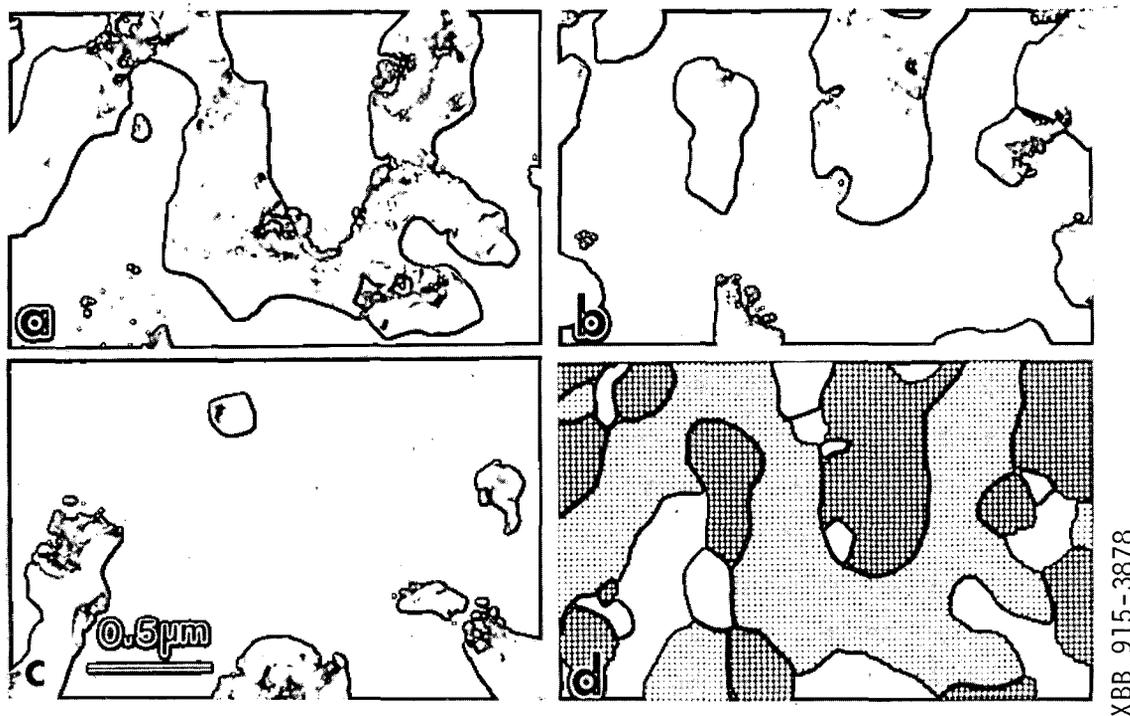
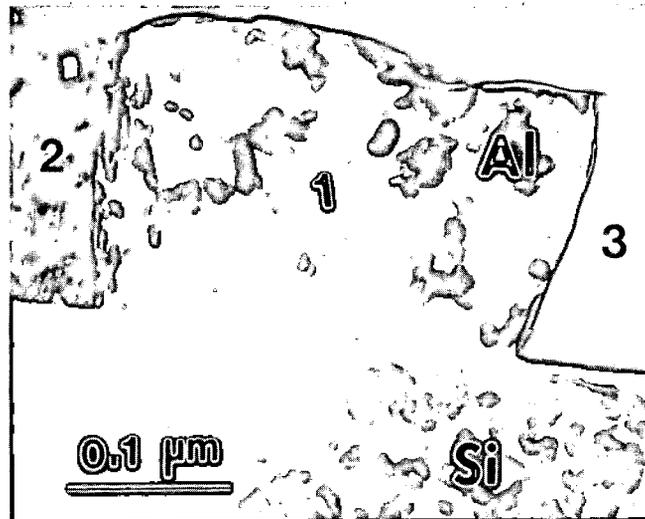
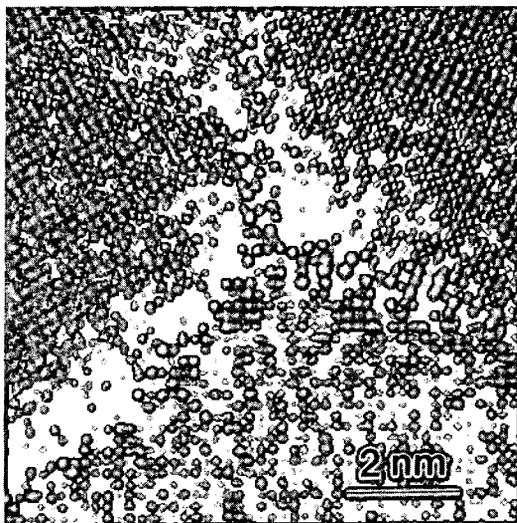


Fig. 6 Series of micrographs illustrating the tricrystal microstructure. (a)-(c) dark field images of the three orientation variants; (d) tracing showing the distribution of the three grain orientations. White areas are remaining grains in the minority (111) orientation.

Fig. 6 illustrates the typical microstructure in three dark field images taken from the same area, showing that the three orientation variants cover almost the entire area. A tracing of the three dark field images, seen in (d) with each orientation variant characterized by different cross hatching shows that the three grain orientations form an interlocking structure with both dual and triple junctions. Only a few small grains remain white in this tracing. These grains were in the minority (111) orientation, also detected by X-ray diffraction, and their volume fraction is sufficiently small to be ignored in the remainder of the analysis.

Although perhaps not immediately apparent from fig. 6, this continuous tricrystal microstructure is unique. Because all grains are related to each other by 120° (or 30°) rotation, the misorientation is identical across any of the grain boundaries. Because all grains close on

themselves, each boundary is free to take on any inclination, but the misorientation remains fixed through the symmetry constraints imposed by the substrate. This results in a unique geometry where triple junctions can be composed of three identical boundaries. Fig. 7 shows a high resolution micrograph of such a triple junction. The lattices of the three crystals are seen along their common $\langle 100 \rangle$ zone axis. The boundaries meet at approximately 120° and each boundary continues along a symmetry plane of the opposing crystal. A full study of the atomic structure and crystallography of this continuous tricrystal microstructure is presently underway.



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Fig. 7 High resolution micrograph of a triple junction where three identical grain boundaries meet at about 120° . All three grains are in $\langle 100 \rangle$ zone axis orientation and misoriented by 30° .

Fig. 8 Cross section conventional micrograph of (100) textured Al film on (111) Si substrate showing the three grains, marked 1, 2 and 3. Grain boundaries are seen to be nearly perpendicular to the substrate. No interface layer is apparent at this resolution level.

A cross section micrograph of a tritextured film is given in fig. 8. It shows a film of approximately 200 nm thickness with the three orientation variants separated by grain boundaries that are nearly perpendicular to the substrate. The substrate/metal interface is relatively flat and no interdiffusion or interfacial reaction is immediately apparent. However, this result must be considered preliminary because only one area of such an interface has been imaged to date. The precise structure and chemistry of this interface is under detailed study because it is likely to hold the clue to the observed behavior.

DISCUSSION

The results of this study show that it is possible to control the texture of Al films on (111) Si substrates through trace amounts of Cu, diffused into the interface before deposition. The mechanism of this effect is not understood at this point. Three possibilities are: 1) Cu could form an oxide and thereby help reduce any remaining SiO_2 on the substrate, producing a cleaner (111) surface than otherwise obtainable. However, this is thermodynamically unlikely because SiO_2 is more stable than copper oxides. It is also contradicted by the fact that under clean UHV conditions (111) films are observed. 2) Cu could form a silicide at the interface which in turn could affect the nucleation and orientation process of Al during deposition. The epitaxial formation of Cu_3Si has been observed during Cu deposition on Si at room temperature [10]. The silicide is pseudo-hexagonal, forms with its c-axis normal to a (111) Si substrate, and is thought to aid in parallel epitaxial growth of Cu. So far, no direct evidence for such a silicide

has been found in this study, and its possible role in promoting (100) over (111) Al growth is not clear. 3) Cu could affect the growth kinetics of Al such that (100) becomes the slowest-growing face and thereby dominates the texture. However, this would not explain the in-plane orientation of the Al. 4) The presence of Cu could affect the surface structure of the substrate. Williams et al. have reported that small amounts of impurities can have a significant effect on the structure and faceting behavior of Si [11]. It has been shown that C and As impurities on Si (111) surfaces influence the structural stability of Si surfaces [12]. These authors recognized the possible importance of this observation in heteroepitaxial growth. Of the possibilities raised here this seems the most likely alternative because only trace amounts are necessary for a large effect. This would agree with the difficulty of detecting Cu in the interface by SIMS experiments. However, further study is necessary before a full understanding of this phenomenon can be obtained and a satisfactory understanding reached. In the meantime, the effect is important in providing a simple means for fabricating the unique continuous tricrystal structure essential in the study of grain boundaries in metals.

CONCLUSIONS

The study of vapor-deposited thin films of Al on (111) Si by X-ray diffraction and transmission electron microscopy has shown that trace amounts of Cu can be used to control the texture during thin film growth of Al on (111) Si substrates. Under UHV conditions and without Cu impurities, Al grows with parallel epitaxy as a (111) single crystal. During vapor deposition in the presence of Cu impurities the films change to a (100) tricrystal structure. The observed epitaxial relationship is not predicted by geometrical criteria based on lattice mismatch, and it is concluded that small amounts of impurities are another important factor in the control of heteroepitaxial growth.

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