

Study for Bonding Technology by Electroplated Nano porous Cu Structure

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Abstract

The various kinds of the packaging technologies such as 2.nD, 2.5D, 3D are highly studied with the rapid development of miniaturization and high density of semiconductor packaging. This trend increases the importance of fine pitch interconnect. To achieve fine pitch interconnect, Cu-Cu direct bonding or hybrid bonding which has no solder in bonding layer is the promising technologies.

There are some difficulties in the solderless bonding such as the control of bump uniformity, high accuracy CMP (Chemical Mechanical Polishing) process and so on. In particular, the exact surface shape control is the essential issue. To solve these problems, we are proposing Nano porous (NP) Cu materials for interconnect material.

One of the technical challenges is the process for formation of NP Cu μ -bump structure. We are focusing on electroplating process for μ -bump formation. Firstly, we developed the plating chemicals for formation of NP Cu structure. We consider two types of plating chemicals for NP Cu formation, de-alloying and direct porous plating process. For de-alloying process, Cu-Zn alloy bumps were plated, and NP Cu bumps were obtained by de-alloying the Cu-Zn alloy. For direct porous plating process, NP Cu bumps were plated by using unique additives which can form NP structure directly. By using electroplated NP Cu, we studied its various properties, and carried out bonding tests. As the results, NP Cu structure shows unique properties such as electrical conductivity and the hardness, and we consider that these unique properties should widen the bonding process margin. We would like to present our recent research of NP Cu which is promising materials for advanced bonding technology.

Key words

Interconnect technology, Nano porous Cu, Flip chip bonding, Electroplating

1. Introduction

To correspond the trend for miniaturization and high performance of electric devices, various packaging technologies such as 2.5D, 2.nD, 3D and chiplet are being widely studied [1][2], and the importance of flip-chip bonding is increasing. Various bonding technologies such as C4 (Controlled Collapse Chip Connection) technology, C2 (Chip Connection) using Cu pillar + solder cap and TCB (Thermal Compression Bonding) have been widely developed for a long time.

In terms of fine pitch bump formation for flip chip bonding, electroplating technology is an effective technology, and various plating chemicals for bumping process have been developed.

For further miniaturization, SLID bonding (Solid-Liquid Interdiffusion), and solderless bonding technologies such as

*1: Thermal Compression Bonding, *2: Solid-Liquid Interdiffusion

	C4	Cu pillar	TCB ^{*1}	SLID ^{*2} bonding	TCB ^{*1} / Solderless bonding	Hybrid bonding
Image						
Materials	Solder	Cu+Solder	Cu+Solder	Cu+Solder i.e., Low melting point metal	Cu	Cu + SiO ₂
Pitch	>130 μ m	>60 μ m	>40 μ m	>20 μ m	<20 μ m	

Fig. 1 Various bonding techniques for interconnect.

direct Cu bonding and hybrid bonding are under development for mass production to achieve fine pitch and high-density packaging. There are many advantages over solder such as good electrical conductivity, prevention of solder bridging and so on. However, there are also some difficulties for bonding process such as CuO₂ remove, throughput, high cost of CMP (Chemical Mechanical Polishing) and so on. Especially, strict flatness and coplanarity are essential for solderless bonding because there

is no liquidus phase during bonding process.

For improvement above issues, we are focusing on the possibility of Nano Porous (NP) Cu materials which have unique properties like softness, and lower temperature sintering effect, etc. This study is aimed at forming NP Cu materials via electroplating technology and considering the possibility for Cu-Cu bonding process.

2. Experimental

2.1 Fabrication and evaluation of NP Cu

In this work, NP Cu materials are fabricated by electroplating process. For fabrication of NP Cu materials, we chose two methods: 1) NP Cu was obtained directly by additives (hereinafter, this is called Direct Porous Cu (DPC) method) and 2) NP Cu was obtained by de-alloying Zn after Cu-Zn plating (hereinafter, this is called de-alloying method). For DPC method, we prepared azole-type additives which is expected strong interaction on Cu surface in copper sulphate solution. For de-alloying method, Cu-Zn alloy was plated and subsequently de-alloyed by HCl aq. solution. For Cu-Zn plating chemical, mild acidity (around pH 4.0) chemical was prepared to accommodate the conventional photoresists by mixing copper sulphate, zinc sulphate, citric acid, and some organic compounds. For normal Cu plating, sulfuric acid-based copper plating chemical was used. Electroplating was carried out by using two-electrode system. Cu plate or Si wafer which is sputtered the conductive seed layer of Cu 500nm / Ti 100nm was used as cathode. For anode, Cu-P anode was used for the DPC method and normal Cu plating, and insoluble Pt/Ti mesh anode was used for Cu-Zn plating. Current density was 0.2 to 2A/dm² for NP Cu and 5A/dm² for normal Cu. Linear sweep voltammetry (LSV) with 5 mV/sec. of scan rate was used to obtain electrochemical polarization curve and performed by using electrochemical analyzer from BAS. In LSV measurement, electrodes consist of Pt RDE (Rotation Disk Electrode), Pt wire as counter electrode, and Ag/AgCl (3M NaCl) as reference electrode. Firstly, NP Cu was plated on Cu/Ti sputtered Si wafer without bump patterning for evaluation of properties of NP Cu. Secondly, NP Cu for μ -bump was plated by using ϕ 20 μ m patterning wafer. FE-SEM (Field Emission Scanning Electron Microscope) was used for the observation of NP Cu. Cross section treatment was performed by ion milling or FIB (Focused Ion Beam). Four-point probe measurements were performed as the evaluation of electrical conductivity, and the volume of plated film was measured by 3D shape measurement tool by Keyence. The composition of Cu-Zn was estimated by EDS (Energy Dispersive X-ray Spectroscopy).

2.2 Bonding tests and Evaluation

Firstly, the bonding interface and bonding strength were compared by plating normal Cu or NP Cu on Cu plate

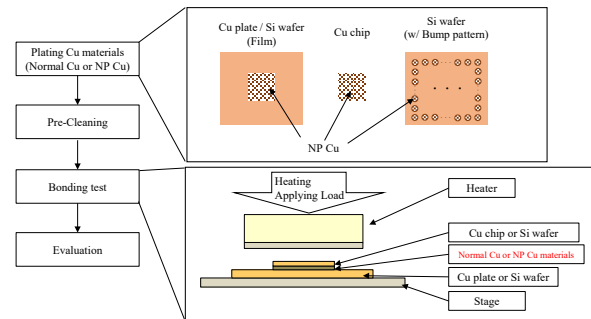


Fig. 2 Schematic image of experimental procedure.

(without patterned). The bonding tests were performed by flip chip bonding tool, and conditions were as follows; the load was 18MPa, the bonding temperature was 370°C, and the bonding duration was 60sec. After bonding, the observation of the interface was performed by FE-SEM, and the shear strength measurement of bonding structure was carried out. For μ -bump test, μ -bump structures which are ϕ 25 μ m were prepared as chapter 2.1 process and the bonding tests and observation were performed by flip-chip bonder as well.

2.3 Consideration for μ -bump bonding process

μ -bump structures were prepared as chapter 2.1, and the bump height and uniformity were measured by laser-triangulation apparatus. The compression depth was compared by PICODENTOR[®] in room temperature. For measuring PICODENTOR[®], ϕ 30 μ m diamond indenter was used, and two samples (20 μ m thickness of normal Cu and 10/10 μ m thickness of NP Cu/normal Cu) were prepared in ϕ 20 μ m pattern.

3. Results and Discussion

3.1 Fabrication of NP Cu by DPC method

Fig. 3 shows SEM images of normal Cu and NP Cu by DPC method from surface and cross-section. Normal Cu and NP Cu were fabricated on the Cu/Ti sputtered Si wafer. From surface images of Fig. 3 b), NP Cu plated film shows unique nanowire-like and porous-like structure. From cross-section image of Fig. 3 c), contrast based on crystal grains was observed with the normal Cu. On the other hand, crystal grains could not be observed from cross-section image of Fig. 3 d). Therefore, crystal grains of NP Cu were small enough to form nano porous-like structure. To consider the mechanism of formation in DPC, electrochemical measurement was performed. Fig. 4 shows electrochemical polarization curves. In Fig. 4, additives for DPC seemed to suppress the reaction compared to the conventional additives for normal Cu although the concentration of Cu²⁺ was the same. Thus, it is considered that the grain growth of Cu crystal was strongly suppressed by the adsorption of the additive component on the NP Cu surface, and nano

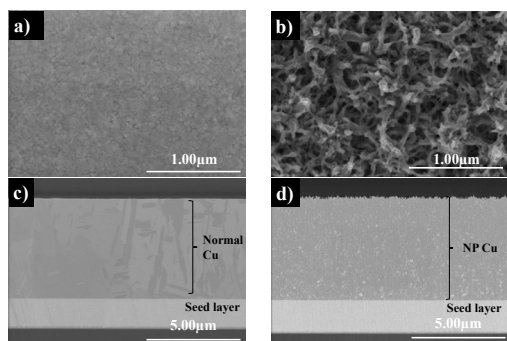


Fig. 3 FE-SEM images of Normal Cu and NP Cu films by DPC; a) Normal Cu surface, b) NP Cu surface, c) Normal Cu cross-section, d) NP Cu cross-section.

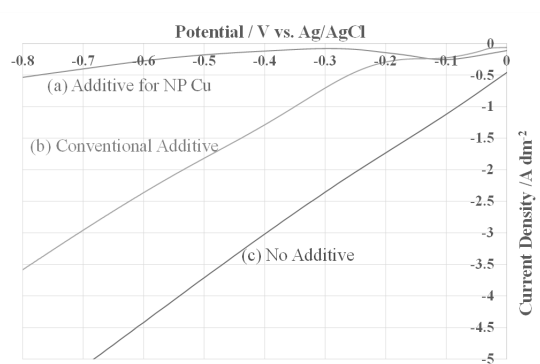


Fig. 4 Electrochemical polarization curves; (a) for DPC, (b) for conventional additive (Normal Cu), (c) for No additive.

Table 1 The Comparison value of Porosity.

Item	Normal Cu	NP Cu
Porosity (%)	0%*	15%

* Ideal data [5]

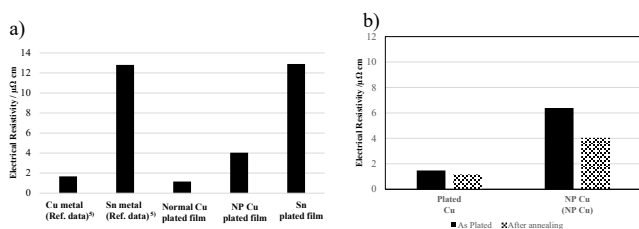


Fig. 5 The results of electrical resistivity; a) the comparison between Cu, Sn, NP Cu, b) the effect of annealing in formic acid of normal Cu and NP Cu.

porous-like structure was obtained by the strong suppression of Cu deposit. Then, the density of NP Cu was estimated by measuring the volume and weight of electrodeposit. The porosity was calculated by following formula (1) by using the volume and weight of electrodeposit, and the density of Cu (8.94g/cm^3).

$$\text{Porosity (\%)} = 100 - \frac{\text{Weight of electrodeposit}}{\text{Volume of electrodeposit}} \div 8.94 \times 100 \quad (1)$$

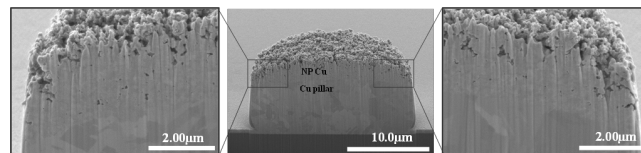


Fig. 6 Cross-section SEM images of NP Cu bump by DPC.

Because of the formation of nano porous structure in the NP Cu film, the film density was lower than that of the normal Cu film. Estimated porosity shows in Table 1. The porosity of NP Cu film was estimated around 15%. For the comparison of electrical properties of the deposit, the electrical resistivity was measured by four-point probe measurement. Fig. 5 shows the comparison of electrical resistivity of NP Cu and normal Cu on the Cu/Ti sputtered Si wafer. The literature values [5] of the specific resistance of Cu and Sn are also in Fig. 5. Cu and Sn are the main materials for bump connection. The electrical resistivity of NP Cu increased four times compared to normal Cu in Fig. 5. It is considered that NP Cu has more grain boundaries and tiny porous structure derived from nano porous structure compared to normal Cu, and this leads to increase the electrical resistivity. On the other hand, when compared with Sn, which is a typical solder material for bumping connection, NP Cu has a lower electrical resistivity and that is expected to have advantage in terms of electrical characteristics. Fig. 5 b) shows the comparison of electrical resistivity of NP Cu and normal Cu after annealing in formic acid atmosphere. The electrical resistivity of NP Cu was decreased after annealing. It is suggested that the annealing treatment will reduce the electrical resistivity of NP Cu. From these results, it is expected that the grain boundaries and tiny porous structure will be decreased due to sintering effect and the electrical resistivity should be decreased after bonding process.

Next, NP Cu was plated by using μ -bump pattern. The design of μ -bump pattern was $\phi 20\mu\text{m}$ in diameter on the Cu/Ti sputtered Si wafer. Firstly, normal Cu was plated and then $3\mu\text{m}$ NP Cu was plated on normal Cu pillar. Fig. 6 shows the cross-section image by FIB-SEM. NP Cu could be obtained in μ -bump pattern.

3.2 Fabrication of NP Cu by de-alloying method

As another fabrication method for NP Cu formation, de-alloying method via electroplating was considered. We chose Cu-Zn alloy as the precursor of de-alloying. Firstly, Cu-Zn alloy was plated, and then NP Cu was obtained by de-alloying Cu-Zn alloy around 3600sec. in 3M HCl aq. solution. Fig. 7 shows the surface and cross-section SEM images of NP Cu by de-alloying method. From surface image in Fig. 7 a), nano porous structure was observed by de-alloying method as DPC method. From cross-section image in Fig. 7 b), the structure of NP Cu by de-alloying

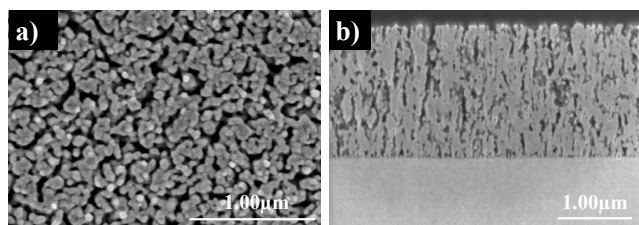


Fig. 7 SEM images of NP Cu films by de-alloying; a) NP Cu surface, b) NP Cu cross-section.

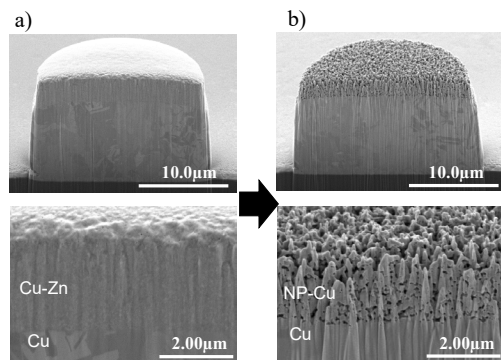


Fig. 8 Cross-section SEM images of NP Cu bump by de-alloying; a) As-plated, b) After de-alloying

method seemed to be different structure compared to DPC method. Compared the cross-section images between DPC method and de-alloying method, NP Cu obtained by de-alloying seemed to have much porous areas and the near open pore structure compared to that by DPC method. The porosity was estimated around 25% by the precursor composition (Cu/Zn) and the results of image analysis of cross-section SEM image. Since the porosity and Cu/Zn composition are almost the same value, it is assumed that Zn was dissolved, and the dissolved area became the porosity structure. It is considered that the difference in the structure of NP Cu by DPC method and de-alloying method was related to the NP Cu formation process. In the case of DPC method, NP Cu structure was formed as bottom-up deposition by additive control. On the other hand, in the de-alloying method, since the film was etched by acid from the outer peripheral area, it is considered that the structure was close to the open pore.

Next, NP Cu was plated by using μ-bump pattern similarly. The design of μ-bump pattern was $\phi 20\mu\text{m}$ in diameter on the Cu/Ti sputtered Si wafer. Firstly, normal Cu was plated and then 3 μm thick Cu-Zn alloy (Cu:Zn=around 80:20at%) was plated on normal Cu pillar, followed by de-alloying. Fig. 8 shows the cross-section image by FIB-SEM. NP Cu could be also obtained by the de-alloying process in μ-bump pattern.

3.3 The bonding tests by NP Cu plating film

The bonding tests were performed by using NP Cu plating

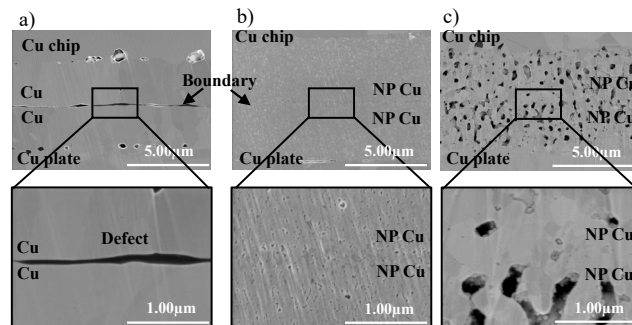


Fig. 9 The comparison of cross-section after bonding; a) Normal Cu, b) NP Cu by DPC, c) NP Cu by de-alloying.

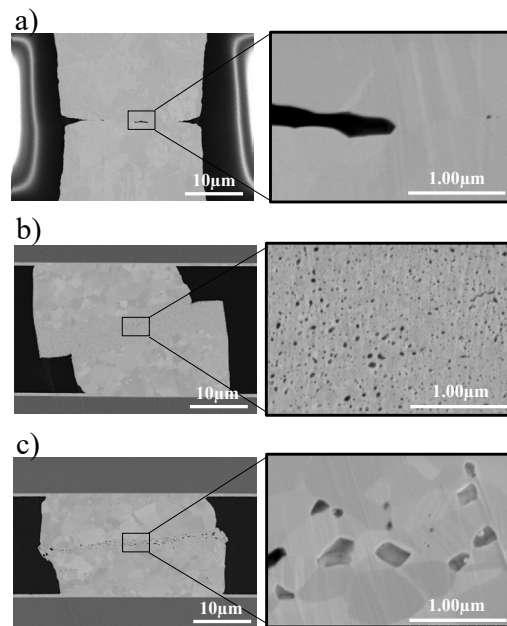


Fig. 10 Cross section image of μ-bump bonding; a) Normal Cu, b) NP Cu, c) NP Cu by de-alloying.

film fabricated by the DPC method and the de-alloying method. Firstly, NP Cu prepared on the Cu/Ti sputtered Si wafer without patterning. Then, the bonding tests and the evaluation were performed as Fig. 2. Before the bonding tests, the surface oxide layer was removed by 10wt% H_2SO_4 aq. without any flattening treatment. After bonding tests, the interface was treated by ion milling, followed by the observation by FE-SEM. Fig. 9 shows the SEM images of the comparison of cross-section after bonding. Defects were observed near the boundary in the case of normal Cu, and it was caused by mismatch of the joint interface due to the surface roughness and the hardness of Cu. In the case of NP Cu, defects were well reduced. It is presumed that both the softness of NP Cu and the sintering effect of nano porous promoted the bonding. At the bonding interface by the de-alloying method (Fig. 9 c)), it seemed that the sintering of nano porous progressed after bonding, although many NP

Cu and vacancies were mixed before bonding due to de-alloying process. Compared the degree of sintering of NP Cu prepared by the DPC method and de-alloying method, the coarse crystal grains were observed at the interface of the NP Cu by the de-alloying method. The shear strength of NP Cu was 50-80MPa even when the DPC method and de-alloying method while the bonding strength of normal Cu was around 20MPa. Although it is necessary to reduce the temperature and the load during the bonding process, it is considered that NP Cu materials will achieve denser bonding interface and improve the bonding strength.

3.4 The bonding test examples of NP Cu μ -bump

To consider the possibility of NP Cu for the bonding materials, the bonding tests by using NP Cu bump were performed. The structure of NP Cu/Cu pillar were prepared by electroplating and then the bonding tests were carried out by flip-chip bonding tool. After the bonding, cross-section treatment was performed by ion-milling, followed by the observation by FE-SEM. Fig. 10 shows the cross-section images of μ -bump bonding. From Fig. 11, the bonding structures of NP Cu have few defects due to the surface shape in both the DPC method and de-alloying method compared to that of normal Cu. This trend was like Fig. 9 and NP Cu is expected to be an effective method for improving the defects in the bonding process. On the other hand, the bonding interface by using normal Cu showed the surface irregularities and height variations because CMP process was not performed in this work, and it is suggested that normal Cu could not relief the variation in the bonding interface. Surface treatment in CMP is a problem in semiconductor processes where the density and miniaturization are increasing. Shape followability of NP Cu is promising candidate for a technology that improves the margin in the CMP process.

3.5 The consideration of effectiveness of NP Cu

Fig. 11 shows the example of bump height uniformity of Cu pillar and NP Cu/Cu pillar structure in the test chip pattern. From Fig. 11, cop. value was the difference between maximum height and minimum height, and Cu pillar structures have bump height variation. In this chapter, NP Cu was prepared by the DPC method. It is supposed that these differences need to be flattened or controlled precisely because there is not liquidus phase in solderless bonding process even if the other factors such as warpage of substrate or wafer are not considered. To assume the margin of NP Cu for bonding process, the compression test was carried out by using PICODENTOR[®] for demonstration. Fig. 12 shows the compression test result of NP Cu bump. From Fig. 12, it was assumed that NP Cu structure can be compressed at about 30MPa and plateau region was appeared. Table 2 shows the measurement result of bump height and diameter of NP Cu

Table 2 The comparison of height and diameter of NP Cu.

	Before compression	After compression	Variation
Bump height(μ m)	22.1	17.2	4.9
Diameter (μ m)	19.7	19.7	0.0

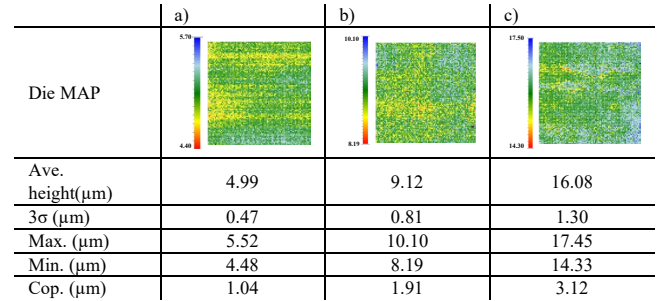


Fig. 11 The results of bump height uniformity measurement; a) 5 μ m normal Cu, b) 10 μ m normal Cu, c) 5/10 μ m NP Cu/normal Cu.

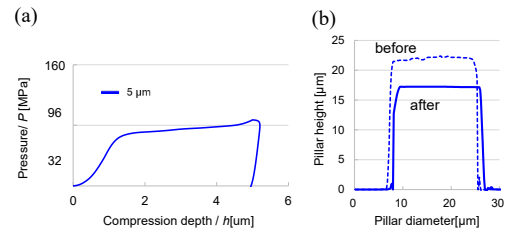


Fig. 12 The result of compression test of NP Cu bump; a) Pressure vs. compression depth curve, b) Bump shape profile.

bump after compression test. From this result, there was the possibility that NP Cu could be compressed around 5 μ m without collapse. Although the compression pressure needs to be decreased by optimizing NP Cu structure, this unique feature of NP Cu should help to widen the process margin and consider the design of materials for the bonding process.

4. Future Study

We found that NP Cu materials have unique properties of nano-sintering effect, bump compression behavior and shape followability. Nano-sintering effect will help to achieve lower temperature and pressure during Cu-Cu bonding process. Bump compression behavior and shape followability will widen the process margin like CMP process. These features should be one of the solutions for direct Cu bonding and hybrid bonding, where Cu surface oxidation and surface roughness are issues [4]. As further evaluation, the unique properties of nano-sintering and bump compression behavior will be deeply studied. Additionally, optimization of the porous structure through advanced

bonding tests including reliability will lead to apply NP Cu materials to direct Cu bonding and hybrid bonding.

5. Conclusion

In this study, fabrication of two types of NP Cu plating films by electroplating was proposed, the DPC method and the de-alloying method. It was confirmed that the NP Cu has the advantage of electrical property compared to the solder material, and NP Cu has unique properties of nano-sintering effect, shape followability and bump compression behavior. When applied as a bonding material, defects in the interface were decreased by using NP Cu materials. From the bonding tests and compression tests by using NP Cu, shape followability of NP Cu is promising candidate for a technology that widens the margin in the CMP process. We consider NP Cu should be one of the solutions for direct Cu bonding and hybrid bonding.

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