GROWTH OF THE SUBSTRATE CRYSTALS FOR $La_{2-x}Sr_xCuO_4$ THICK FILMS

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Abstract

Single crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) are promising as a substrate to realize superconcuting electronic devices. The distribution coefficients of Ni and Zn to the Cu site in La_2CuO_4 (LCO) were estimated by the zone melting technique to grow high quality single crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn). The distribution coefficient value of Ni was estimated to be 4.2 and that of Zn was estimated to be 0.66, respectively. Suitable solvent compositions were determined using these values to grow single crystals by the traveling floating zone (TSFZ) method. Single crystals of LCO, $La_2Cu_{1-x}M_xO_4$ (M=Ni(x=0.01, 0.02, 0.03, 0.04), Zn(x=0.01, 0.02, 0.03)) of high homogeneity were grown. The behaviors of the magnetization of these as-grown crystals do not indicate superconductivity except LCO. Ni or Zn substitution can make LCO non superconductor. This fact suggest that single crystals substituted by Ni or Zn are useful as substrate crystals.

Introduction

High quality single crystalline films in the thickness of μm order on non superconducting substrate crystals are desired to realize the superconducting electronic switching devices in THz region. The selection of the substrate is one of the important factor to realize such films. The main features desired for substrate crystals are high lattice matching with superconducting films and non-superconductivity.

In this paper, we tried to search for more suitable substrate crystals to grow high temperature superconducting single crystalline films of $La_{2-x}Sr_xCuO_4$(LSCO). La_2CuO_4 (LCO) was focused from the point of view of lattice matching because LCO was well known as the mother compound of LSCO. LCO has another advantage because it is not a superconductor but a insulator in its stoichiometric composition [1]. However, excess oxygen easily dissolve into crystals. 1 % excess oxygen make LCO a superconductor [2]. This feature is a weak point as a substrate. When small amount of an impurity such as Fe, Co, Ni, Zn, Ga, and Al is substituted to Cu site, Superconductivity of LSCO is drastically suppressed [3]. To find a way out of the weak point of LCO as a substrate, impurity substitution was examined. In this study, Zn as an non magnetic element and Ni as a magnetic element were selected for impurity elements.

At first, growth condition was investigated. The distribution coefficients of Ni and Zn are estimated by zone melting technique and estimated to be 4.2 and 0.66 respectively. Suitable composition of solvents were determined by the values of the distribution coefficients. Using suitable solvents, single crystal of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) or La_2CuO_4 could be grown. Magnetic properties of all grown crystals except LCO were found to be non-superconductor even after annealing in oxygen atmosphere. These results suggest that these crystals may be useful as substrates for LSCO films.

Experiment

La_2O_3(> 99.99%), CuO(> 99.9%), ZnO(> 99.99%), NiO(> 99.9%) powders were used as raw materials. These powders were weighted out in molar ratio to prepare La_2CuO_4, $La_2Cu_{1-x}M_xO_4$ (M = Ni (x=0.01, 0.02, 0.03, 0.04), Zn (x=0.01, 0.02, 0.03)) and were mixed with ethanol. The mixtures were fired at 850°C for 12 h in the oxygen flow condition and ground. The objective powders were obtained after second firing and regrind. The objective materials were put into rubber tubes to form rods and pressed. Pressed rods were sintered at 1240±20°C for 12 h in oxygen flow atmosphere to obtain feed rods. For solvents, raw materials were weighted out in molar ratio of 78~80 mol% (CuO_{1-x}+M_xO(M=Ni, Zn)) and fired in the same way.

The relationships between chemical composition of the substituted element in solid and that in liquid were investigated to estimate the suitable solvents composition. Using the zone melting technique, distribution coefficients of substituted elements were estimated. For both substitution elements Ni and Zn, Crystals were grown using feed rods(x=0.03) and solvents (x=0.03). The chemical compositions of grown crystals were analyzed along growth direction from seeding points. The distribution coefficients of Ni and Zn were estimated by the analysis of their concentrations as a function of growth length. Using the values of the distribution coefficients, suitable composition of solvents were determined and crystals were grown. The chemical composition of grown crystals were analyzed along the growth direction and within the section of grown crystals to check the homogeneity of grown crystals. The chemical analysis of grown crystals was performed using X-ray micro analyzer (XMA: JEOL Co., model JXA-8600M).

Magnetic property of grown crystals were measured by superconducting quantum interference device (SQUID: QUANTUM DESIGN Co., model MPMS-5S).

Result and Discussions

Figure 1 indicates the results of the chemical analysis of crystals along growth direction which were grown using feed rods of x=0.03 and solvents of x=0.03. Figure 1(a) corresponds to Ni substitution and Figure 1(b) to Zn substitution. In the case of the Ni substitution Fig. 1 (a), Ni concentration at the neighbor of the seeding point is about x=0.125, which is higher than that of feed rod and solvent. However Ni concentration gradually reduced down to x=0.03. This fact means that the distribution coefficient of Ni is larger than unity and that the solvent of less Ni concentration is more suitable for crystal growth of higher homogeneity. In Zn substitution Fig. 2(b), Zn concentration is 0.02 which is lower than that of feed rod and solvent. However, Zn concentration gradually increased up to the Zn concentration of the feed (x=0.03) These fact means that the distribution coefficient of Zn is smaller than unity and that the solvent of higher Zn concentration is more suitable.

When the distribution coefficient is assumed to be constant, which means, the distribution coefficient is independent of the concentration of the substituted elements, the concentrations of crystals which are grown by zone melting technique can be expressed like

$$\frac{c}{c_0} = 1 - (1-k)e^{-k\frac{x}{L}} \tag{1}$$

k is the distribution coefficient, c is the concentration of the substituted element in the grown crystal. c_0 is that in the feed rod. L is the zone length (4 mm). x is the length from the growth starting point [4]. Equation (1) can be modified like

$$\ln\left|1 - \frac{c}{c_0}\right| = \ln|1-k| - k\frac{x}{L} \tag{2}$$

Therefore when $\ln(1\text{-}c/c_0) = \ln(1\text{-}k)$ is plotted as a function x/L, the distribution coefficient can be known by the slope of this plot. Figure 2 show the plots. The distribution coefficients of Ni and Zn were found to be 4.2 and 0.66, respectively.

When the distribution coefficient is k, the relationship between the concentration of solvent c_0 and that of the grown crystal c can be expressed like $c = k\, c_0$. Using this relation we can estimate suitable composition of solvent can be determined. The compositions of feed rods and solvents used in this experiment were summarized in table I. In table I, average values of analyzed composition for grown crystals were also shown. The photographs of crystals by TSFZ were shown in Fig. 3. Grown crystals were black and metallic luster is recognized on the surface. It was found that the grown crystals were single phase and have no grain, sub-grain by the polarized optical microscope observation.

The distribution of chemical composition along growth direction from seeding points were shown in Fig. 4. For all crystals, the chemical compositions of grown crystals even at the initial part were consistent with that of feed rods. This result means each chemical composition based on the distribution coefficient were suitable for each crystal growth.

Figure 5 shows the chemical analysis within the section of the initial part (open symbol) and final part (closed symbol) of the grown crystals respectively and indicates the uniform distribution of the chemical composition even in the sections. However, slight inhomogeneity was recognized for the crystals substituted by Ni. In the crystals of x = 0.03 and 0.04, the center regions of the section of the final part indicate slightly lower Ni concentration and the fringe regions indicate higher Ni concentration. The reason of the distribution is at present unknown.

Magnetic property of grown crystals were shown in Fig. 6. In LCO, diamagnetic signal accompanied by superconducting transition was observed. However, No diamagnetic signal were observed for all crystals substituted by Ni and Zn This behaviors did not changed even after the annealing under the oxygen flow atmosphere. Non-superconductivity of the crystals substituted by Ni or Zn is useful as substrate crystals for superconducting film growth. As ionic radius of Ni and Zn are quite similar to that of Cu, these crystals is expected to have good lattice matching with LSCO. Therefore Ni or Zn doped LCO crystals may be the best substrate crystal to grow LSCO film on it.

Conclusion

The distribution coefficients of Ni and Zn for La_2CuO_4 (LCO) were examined by zone melting technique and found to be 4.2 and 0.66 respectively. Using distribution values, suitable solvent composition were determined to grow single crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni (x = 0.01, 0.02, 0.03, 0.04), Zn (x = 0.01, 0.02, 0.03)). Single crystals were grown by TSFZ method. Chemical compositions of grown crystals were found to be uniform all over the grown crystals and to be consistent with the feeds. No diamagnetic signals, which represent superconductivity, were observed for all grown crystals except LCO. Same results were obtained for crystals annealed in oxygen atmosphere. This result means that Ni or Zn substitution is useful to make LCO non-superconductor. These results suggest that LCO single crystals substituted by Ni and Zn may be useful as a substrate crystals for the growth of LSCO films.

Acknowledgement

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Table I Chemical composition of feed rods, solvents and grown crystals

	Nominal Composition		Analytical Composition	
	Feeds (x)	Solvents (x)	Grown Crystals (x)	
			Initial part	Final part
Ni	0.01	0.002	0.009 (1)	0.010 (1)
	0.02	0.005	0.020 (1)	0.020 (1)
	0.03	0.007	0.030 (1)	0.030 (1)
	0.04	0.010	0.041 (1)	0.040 (1)
Zn	0.01	0.015	0.010 (1)	0.010 (1)
	0.02	0.030	0.020 (1)	0.020 (1)
	0.03	0.045	0.030 (1)	0.030 (1)

Figure captions

Figure 1. The distribution of the substituted elements (M= Ni, Zn) in $La_2Cu_{1-x}M_xO_4$ grown crystals along the growth direction. Both chemical compositions of feed rods and solvents were x=0.03.

Figure 2. $\ln(1-c/c_0)$ or $\ln(c/c_0-1)$ as a function of x/L. The slopes of these plots were corresponds to the distribution coefficient (k).

Figure 3. The photographs of grown crystals of $La_2Cu_{1-x}M_xO_4$ (M= Ni, Zn).

Figure 4. The chemical composition of the substituted elements in grown crystals along growth direction.

Figure 5. The chemical composition of the substituted elements within the sections of grown crystal rods.

Figure 6. The temperature dependence of the magnetization for as-grown crystals of $La_2Cu_{1-x}M_xO_4$ (M= Ni, Zn) and La_2CuO_4.

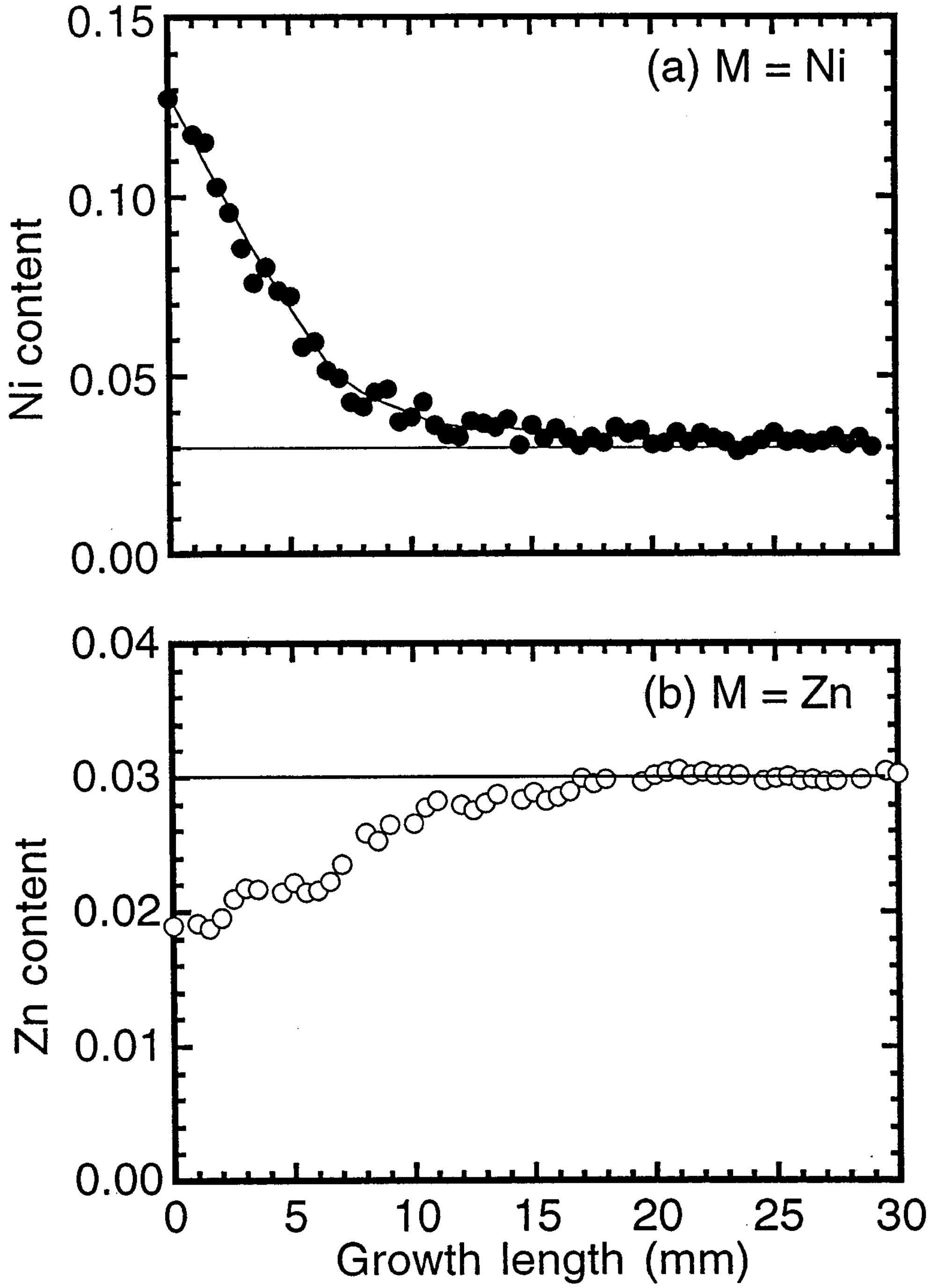

Figure 1. Watauchi *et al.*

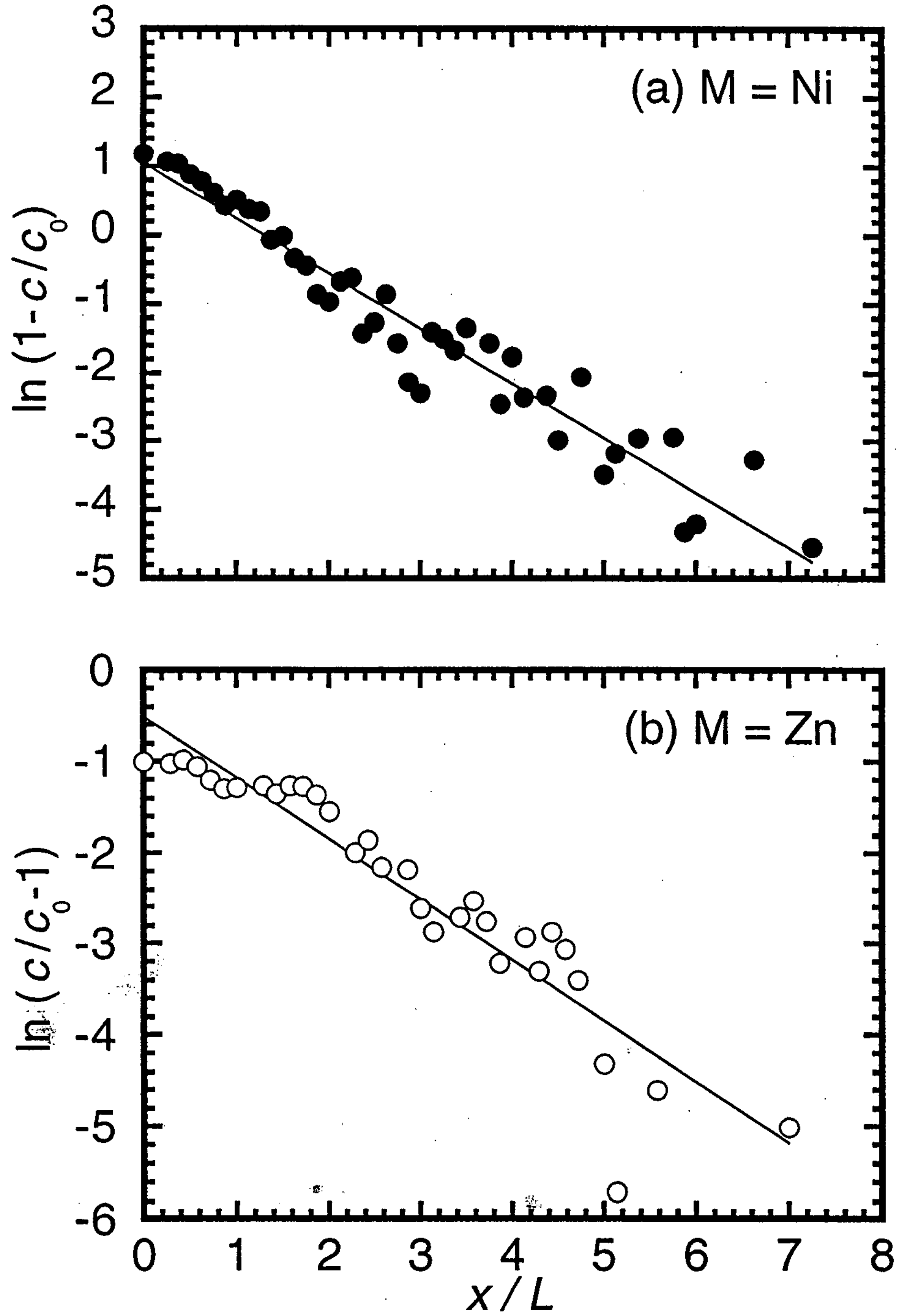

Figure 2. Watauchi *et al.*

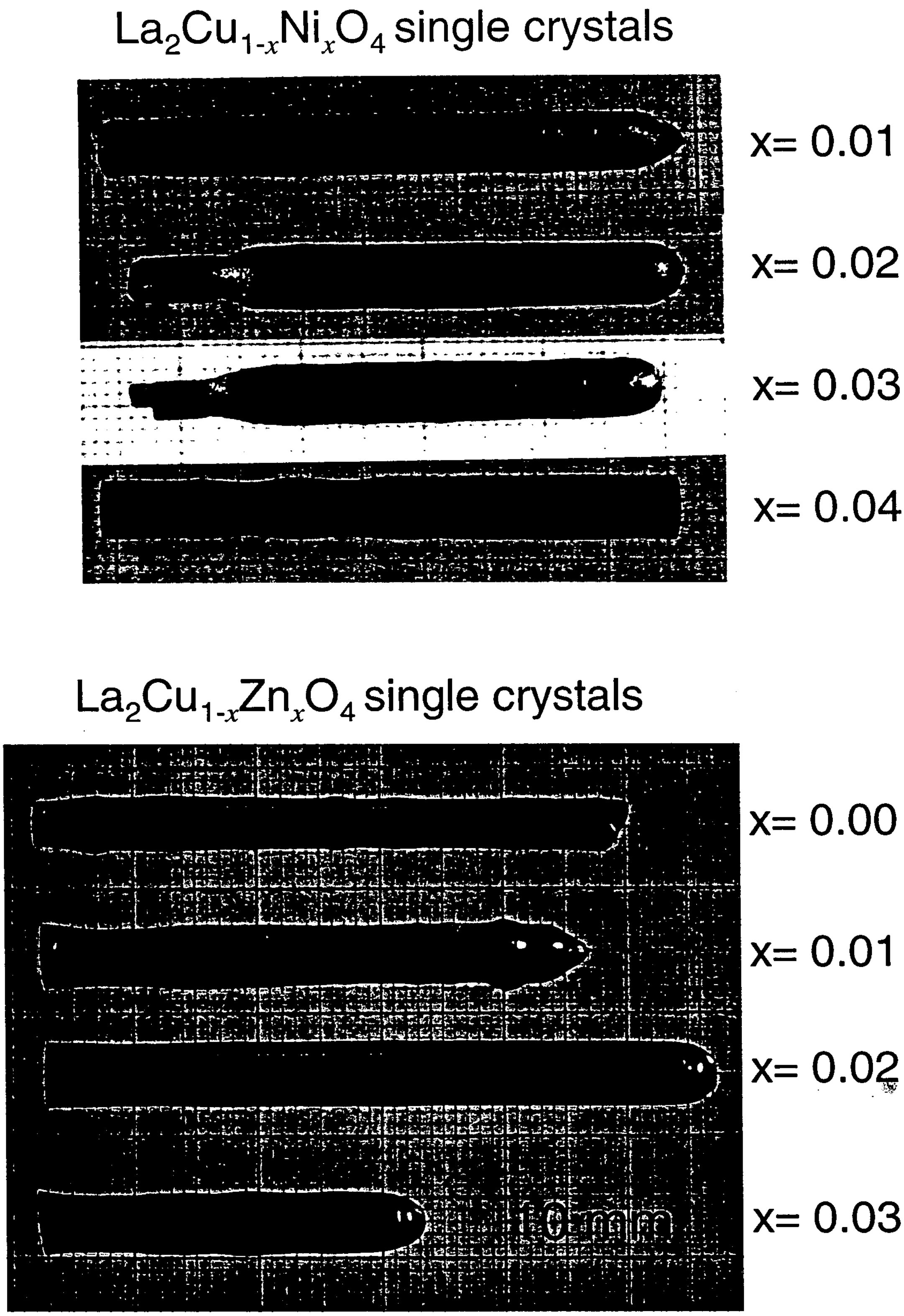

Figure 3. Watauchi *et al.*

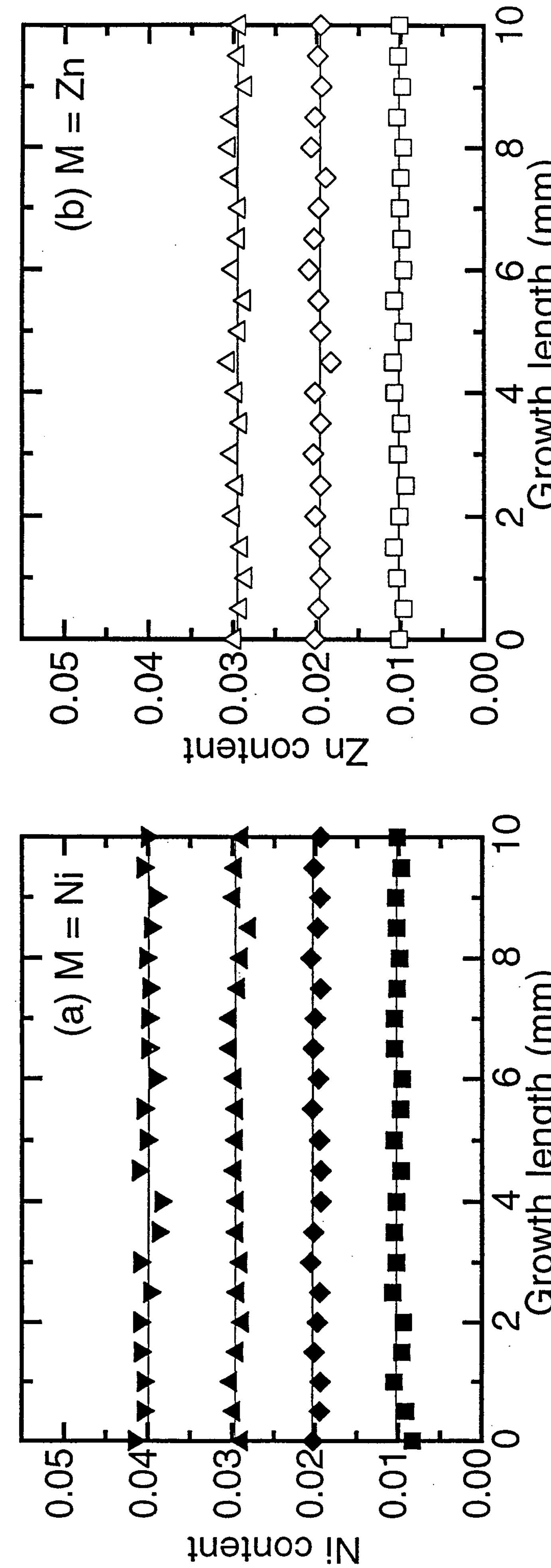

Figure 4. Watauchi *et al.*