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THERMAL DEGRADATION OF NiPt GERMANOSILICIDE FILMS FORMED ON UNDOPED AND DOPED SiGe SUBSTRATES

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ABSTRACT

With the continuous scaling down the VLSI technology, there is an escalating interest in SiGe alloys for performance enhancement of the MOSFETs transistors, since SiGe films can be present in the gate and source/drain areas of MOSFETs. In this work NiPt germanosilicides were fabricated with 20 nm thick Ni and different Pt layer (3, 6, 9, and 12 nm thick) by rapid thermal annealing (RTA) at 300 ºC, and then the post-annealing effects on these samples were investigated in the temperature range between 400 ºC to 750 ºC. The obtained silicide samples were characterized by four point probe method, grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy with field emission gun (FESEM) and atomic force microscopy (AFM). Smooth and uniform Ni (Pt) monogermanosilicide films have been observed for all analyzed samples. For annealing temperatures lower than 500 ºC the samples exhibited thermal stability with sheet resistances of 10 – 30 Ω/sq, and sheet resistance degradation for annealing temperatures of 500 ºC and above. Structural transformation of the formed silicide to Ge rich Ni(Pt)$Si_{1-u}Ge_u$ films was found to occurs with increasing of the annealing temperature. Surface analysis revealed morphological instability of germanosilicides and strong tendency for agglomeration and mounds-like structure formation, which leads to an abrupt increase in the sheet resistance.

1. INTRODUCTION

Silicides have been widely used in complementary metal oxide semiconductor (CMOS) technology to reduce the resistance of gate and source/drain regions. SiGe alloys offer significant potential applications in the fabrication of high-speed electronic and optoelectronic devices [1-4]. For the $Si_{1-x}Ge_x$ device applications, a metallic-like/ $Si_{1-x}Ge_x$.
contact fabricated using a technology similar to the salicide (self-aligned-silicide) process plays a key role for the proper operation of the circuits [5]. Recently, the interfacial reaction of metal/ $Si_{1-x}Ge_x$ have been studied for many metal films. A ternary compound is generally formed as Ge segregation has been observed at annealing temperatures above 400 ºC depending on the total amount of Pt. As Ge segregation will degrade the contact performance significantly, a low temperature annealing for the silicidation process by Rapid Thermal Annealing (RTA) to reduce Ge segregation is preferred for future SiGe based devices. Two major concerns with NiSi are its poor phase and morphological stability under thermal stress in the presence of excess Si, wich is often the case for contacts on Si, thin films of NiSi react with Si to form $NiSi_2$ at 750-800 ºC [6]. On polycrystalline Si substrates, continuous NiSi films break up into discrete NiSi at 550 ºC and layer inversion may occurs upon further annealing temperature [7]. Alloying Ni and Pt results in an appreciable increase in temperature for the formation of $NiSi_2$ and noticeably improves morphological stability of NiPt/Poly-Si layered structure [8-9].
Since $Si_{1-x}Ge_x$ films can be present in the gate and source/drain areas of metal-oxide-semiconductor field-effect-transistors (MOSFETs), the solid-state interaction between Ni, Pt and $Si_{1-x}Ge_x$ is a matter of the utmost importance [10-11]. In recent works, the formation temperature of $NiSi_2$ is increased from 750 ºC to above 850 ºC as a result of the formation of a ternary solid solution $NiSi_{1-u}Ge_u$ when reacting Ni with poly-$Si_{1-x}Ge_x$ films. However, the morphological stability of a $NiSi_{1-u}Ge_u$/poly-$Si_{1-x}Ge_x$ film stack is notably worse than that of a NiSi/poly-Si film. The morphological degradation is further worsened when the Ge fraction in $Si_{1-x}Ge_x$ is increased. On the other hand the use of Ni(Pt) alloy has been shown to improve the stability of Ni(Pt) on SiGe up to 900 ºC by minimizing agglomeration and retarding the formation of the high resistivity $NiSi_2$ phase [12].
In this work, we study the stability and morphology degradation of Ni silicide films on undoped and doped poly-$Si_{0.7}Ge_{0.3}$ prepared with a thin Pt interlayer. The understanding of thermal stability is of great interest for device applications, because it limits the allowed thermal budget for further processing. Thus, the thermal stability was investigated as a function of the post-silicidation annealing temperature using a variety of characterization techniques.

2. EXPERIMENTAL DETAILS

In order to grow the $Si_{1-x}Ge_x$ films, a 2 inches Si(100) n-type Silicon wafer previously cleaned by a standard RCA method was used. At first a 300 nm of thermal SiO_2 was grown followed by the deposition of 600 nm(measured by elipsometer method) thick undoped poly-$Si_{1-x}Ge_x$, grown by Low Pressure Chemical Vapor Deposition (LPCVD) tech-

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nique, using hydrogen diluted SiH_4 and GeH_4 at pressure of 5 Torr and temperature of 750 ºC with deposition time of 5 minutes. At this step one set of 4 wafers containing poly-SiGe were doped with Phosphorus using an ion implanter 'EATON GA4204', with energy of 50Kev and 1x $10^{16}cm^{-2}$ of dose. After that the substrates were pre-cleaned with acetone and isopropanol solution at 80 ºC for 10 minutes, followed by 30 seconds dip in HF1:10 solution, just before metal evaporation. Different thickness of Pt (3, 6, 9 and 12 nm) and Ni (20nm) were sequentially deposited by e-beam evaporation on top of the $Si_{1-x}Ge_x$ layers at room temperature with a base pressure of 4×10^{-9} Torr, and deposition rate of 0.1 nm/s. The silicidation step to form germanosilicide layers was carried out by RTA process at temperature of 300 ºC for 40 s in a dry N_2 ambient. After the silicide formation, the unreacted Ni and Pt were removed using a aqua-regia (HNO_3 : HCl, 1:3) solution at 80 ºC. The selective etching of metals was checked by the four point probe measurements.

The prepared Ni(Pt)SiGe silicide samples were then cleaved in 8 pieces from the wafers, and each of them subjected to different post-silicidation annealing temperature by RTA, with the temperature varying from 400-750 ºC for 40s in a dry N_2 ambient. The germanosilicide films were characterized by four-point probe technique to measure the sheet resistance, GIXRD with CuKα radiation at fixed incident angle of 0.5º (Philips X`Pert MRD), to identify the phase transformation, FESEM and AFM (DI Nanoscope IIIa, in tapping mode). To analyze the morphology.

3. RESULTS AND DISCUSSION

The sheet resistance variation of the $Ni(Pt)Si_{0.7}Ge_{0.3}$ samples as a function of the post-silicidation annealing temperature, for various thickness of Pt, is shown in Fig.1a for undoped substrates and in Fig.1b for doped ones. For comparison the figure includes also the sheet resistance values of the as-silicided samples. The sheet resistance measured for the "as silicided" samples exhibited low sheet resistance values, for instance in Fig.1a we have 10.8Ω/sq for silicide formed with 12 nm Pt and 14.7Ω/sq for that formed with 3 nm Pt. While in Fig.1b we have a minimum of 5.6Ω/sq for silicide formed with 3nm of Pt and 5.7 Ω/sq for those formed with 6nm of Pt. Since these are the minimum resistance verified among all the evaluated samples, one can assumes that as-silicided samples are already fully silicided, even though the low silicidation temperature of 300 °C. With regard to the thermal stability of post-annealed germanosilicide films, as Fig. 1a shows, the sheet resistance revealed the same degradation pattern for all the samples. In Fig.1b we clearly see the great contribution of Pt to the thermal stability of the resulting silicide. In Fig.1a the sheet resistance gradually increases with the annealing temperature, from about 14.0 Ω/sq to 50.0 Ω/sq in the temperature range of 400 °C to 500 °C. Beyond 500 °C, the sheet resistance of the Ni(Pt) germanosilicide films increases drastically to high resistance values. This critical temperature is reached above 500 ºC for silicide samples formed with 6, 9, and 12 nm of Pt, and above 600º C for 3 nm of Pt. The post-annealed samples preserve the low sheet resistance value, lower than 30Ω/sq up to annealing temperature of 450 ºC, regardless of the used Pt layer thickness in the silicide formation. While in Fig.1b for temperature range of 400ºC to 500ºC the sheet resistance maintain a value very close to 6 Ω/sq, for sample with Pt while for sample without Pt the sheet resistance reach values that varies from 8 to 9 Ω/sq. In the critical temperature range (above 500º) the sheet resistance of the samples without Pt drastically increases. In the other hand the silicides with Pt reach a maximum value of 7.6Ω/sq, at 640ºC.

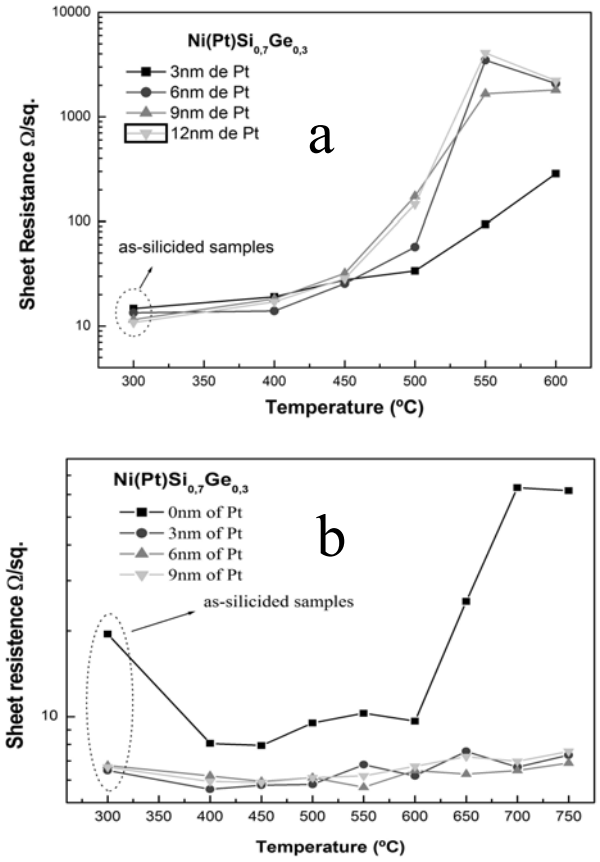

Figure 1 - Sheet resistance behavior as a function of the RTA post-silicidation annealing temperature of Ni (Pt) germanosilicide films, formed on undoped (a) and doped (b) $Si_{0.7}Ge_{0.3}$ with fixed 20 nm Ni and different thickness of Pt.

For the present germanosilicide films prepared with fixed 20 nm thick Ni, samples with 3 nm of Pt exhibited at annealing temperatures above 400-450 ºC, the lowest sheet resistance and better thermal stability in comparison to the silicides formed with more thick Pt layers. The observed sheet resistance degradation can be attributed to the morphological deterioration of $Ni(Pt)Si_{0.7}Ge_{0.3}$ films, which is delayed in Fig.1b, by the fact that the silicides were grown in doped $Si_{0.7}Ge_{0.3}$. Despite the fact that dissolution of Pt retards the formation of the high resistivity phase $NiSi_2$, minimizes the Ge agglomeration and improves the thermal stability of the silicide for temperatures as high as 600 ºC in Si and poly-Si,

on an undoped poly- $Si_{x-1}Ge_x$ the presence of Ge in the substrate degrades the surface morphology of the silicide films significantly. In the lower annealing temperature of around 500–550ºC, the Ge contents in the Ni(Pt) germanosilicide phase is similar to that of the $Si_{0.7}Ge_{0.3}$ substrate. However, at higher annealing temperatures, thermodynamically Ni prefers to react with Si compared to Ge. Consequently Ge segregates out from the germanosilicide grains, and eventually form Ge rich $Si_{1-u}Ge_u$ ($u > x$) between the Ni(Pt) germanosilicide grains. Therefore, the degraded sheet resistance can be possibly due to agglomeration of germanosilicided films or formation of some Ge rich islands or clusters. In Fig.1b the samples with Pt on it, apparently are not affected by the formation of Ge-islands.

Fig. 2a and Fig.2b shows the GIXRD results acquired in the 2θ interval from 20° to 65° of the Ni(Pt) germanosilicide samples prepared with 6nm of Pt, and post-annealed from 400 to 750 ºC. The notations used to index the intensity peaks in the diffractograms refer to Si (hkl) and NiSi (hkl) for simplification, though Ge can be present in the $Si_{1-x}Ge_x$ and $Ni(Pt)Si_{1-x}Ge_x$ solution alloys.

It is clear from the diffractograms that the peaks corresponding to the $Ni(Pt)Si_{1-u}Ge_u$ phases remain at about the same position for the samples annealed at low temperatures of 400 ºC and 450 ºC, and for those annealed at higher temperatures of 700 ºC and 750 ºC. In agreement with Vergard's law, $NiSi_{1-x}Ge_x$ or $Ni(Pt)Si_{1-x}Ge_x$ (with x different from that of the substrate) can be formed because NiSi, NiGe, PtSi, and PtGe have the same orthorhombic crystallographic structure and Pnma space group. From the GIXRD spectra shown in Fig.2, $NiSi_{1-x}Ge_x$ or $Ni(Pt)Si_{1-x}Ge_x$ is the only silicide phase detected for our post-annealed samples in all the temperature range, and no Si rich $NiSi_2$-like phase was detect even at high annealing temperatures of 700 ºC and 750 ºC. In the Ni-Si system it's known however that the low resistivity NiSi phase transforms to higher resistivity $NiSi_2$ phase at annealing temperature exceeding 700 ºC. Hence, we suppose that the presence of Ge in $Si_{1-x}Ge_x$ substrates have the effect of suppressing the formation of disilicide phases in our germanosilicided samples.

The remarkable differences in the diffraction patterns between the samples post-annealed up to 700 ºC and that annealed at 750 ºC are enhancement of Ni(Pt)Si (211) plane, disappearance of Ni(Pt)Si(020) plane and a notable enhancement of Si(311) plane. This result can be explained, in the case of Fig.2a, in terms of Ge content diminishing in the grain/film as the annealing temperature increases, due to the repelling of Ge by Si from the germanosilicided films, since XRD results are average over a large number of grains. The EDS analysis confirms the GIXRD result that Si and Ge atomic composition changes in germanosilicided films at high annealing temperatures. In the other hand the samples with doped SiGe (Fig.2b) appear not to be affected very much by this phase formation. In the undoped case at annealing temperature up to 650 ºC the Ge contents was about 28.0% in the germanosilicided films, so close to that of the $Si_{0.7}Ge_{0.3}$ substrate, whereas at 750 ºC this is reduced to the order of 18.0%. Moreover, the reduction of Ge composition occurs concurrently to the rapid growth of the Ge rich $Si_{1-u}Ge_u$ grains, that precipitates at the germanosilicide grain boundaries, causes agglomeration and degrades the sheet resistance of the layers. Thus, according to x-ray diffraction and EDS results, the degradation of the resistivity of post-annealed germanosilicided films at temperatures above 500-550 ºC, can be attributed to agglomeration and formation of the Ge rich silicide clusters of mounds-like structures.

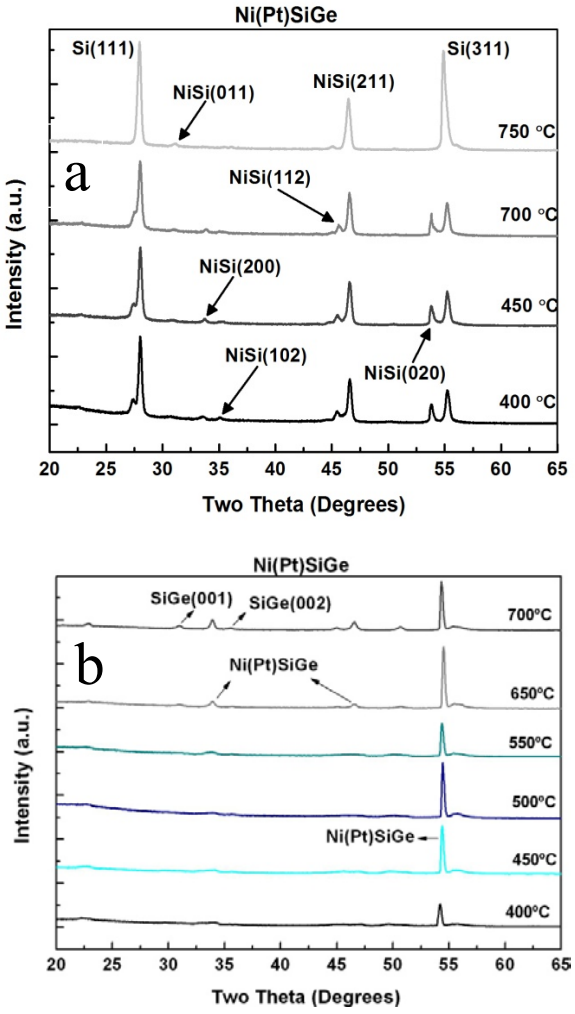

Figure 2 - X-ray diffraction spectra of Ni(Pt) germanosilicided films formed on undoped(a) and doped (b) poly-$Si_{0.7}Ge_{0.3}$ with 20 nm thick Ni and 6 nm Pt, and subjected to different post-silicidation temperatures by RTA

Fig. 3 shows cross section FESEM image of the $Ni(Pt)Si_{0.7}Ge_{0.3}$ sample formed on undoped SiGe, with 20 nm Ni and 6 nm Pt and post-annealed at 450 ºC. As observed from the micrograph, the $Ni(Pt)Si_{1-u}Ge_u$ film forms continuously on the poly-$Si_{0.7}Ge_{0.3}$ layer, apparently without any protrusions. All the analyzed samples revealed uniform $Ni(Pt)Si_{1-u}Ge_u$/poly-$Si_{0.7}Ge_{0.3}$ layered structures at annealing temperatures up to 500ºC, indicating formation of good quality Ni(Pt) germanosilicide films with very low interlayer roughness. The measure silicide layer thickness was ap-

proximately 52 nm for the Ni(Pt) silicide sample formed with 20 nm Ni and 6 nm Pt, and heat treated up to 500 ºC, and about 57 nm for those annealed at 750 ºC, indicating Si to Ni relationship of about 2.6 – 2.8. Assuming thickness of 52 nm, the exhibited resistivity of our samples are 69.7; 72.5; 132.3; and 295.6 μΩcm for as-silicided and post-annealed germanosilicided films at temperatures of 400 ºC, 450 ºC, and 500 ºC, whereas the resistivity of the desired Ni-Si-Ge system is 17-25 μΩcm.

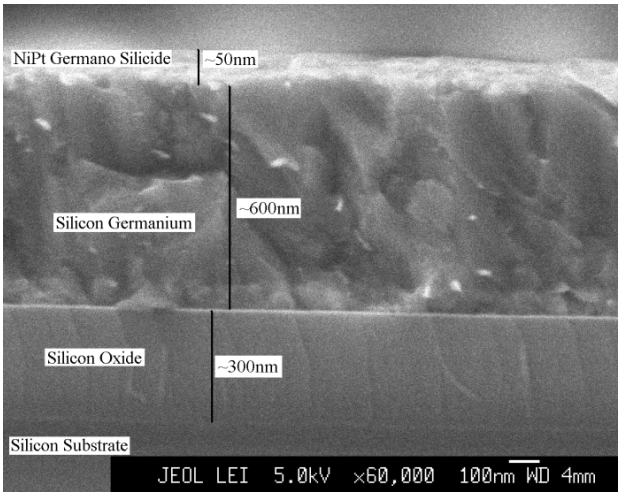

Figure 3 - Cross section FESEM micrograph showing the complete silicide/poly-$Si_{0.7}Ge_{0.3}$/SiO_2/Si structure of the Ni(Pt)$Si_{0.7}Ge_{0.3}$ sample formed with 20 nm Ni and 6nm of Pt and post-annealed at 450 ºC.

The AFM measures for both kind of samples (silicides on doped and undoped SiGe) show us that the rms roughness of the samples stay at or below 2nm. Since agglomeration of a thin silicide film is often accompanied by a severe roughnening of the silicide/SiGe interface, such a low rms roughness can be used to prove the good quality of the silicide produced [13].

4. CONCLUSIONS

This work investigated silicide formation using Ni/Pt bilayer on undoped and doped poly-$Si_{0.7}Ge_{0.3}$ and its thermal stability when subjected to the additional heat treatments at temperature range of 400 ºC to 750 ºC. The results revealed that very uniform and stable Ni(Pt)$Si_{1-u}Ge_u$/ poly-$Si_{0.7}Ge_{0.3}$ layered structures can be obtained at annealing temperatures up to 450 ºC, with rms roughness below 2 nm and low sheet resistances values of about 25.5 Ω/sq for undoped substrates and below 4 Ω/sq for the doped ones. At high annealing temperatures silicide and germanium agglomeration clusters may form, causing morphological degradation and high sheet resistances of the germanosilicided samples. The use of a thin Pt layer enhances the window of the formation temperature to the range of 400-800 ºC and in the case for doped SiGe, the use of Pt increases even more the window of formation. These good results in thermal and morphological stability on poly-$Si_{0.7}Ge_{0.3}$ indicate that the Ni(Pt)SiGe presents a suitable properties to be used as contacts and interconnection lines in sub-micron CMOS device fabrication.

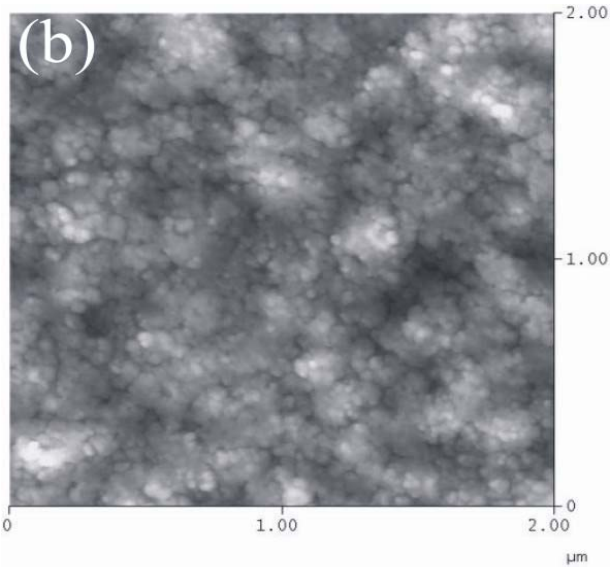

Figure 4 - AFM images of Ni(Pt)$Si_{0.7}Ge_{0.3}$ samples formed with 20 nm Ni and 6 nm of Pt and thermally treated at 400 ºC (a) and 750 ºC (b).

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REFERENCES

1. MAEX, K., *Mat. Sci. Eng. R* 11 (1993) 53-153.
2. KONING, U.; BOERS, A.J.; SCHAFLLER, F.; KASPER, E., *Electron. Lett.* 28 (1992) 160-162.
3. NAYAK, D.K.; WOO, J.C.S.; PARK, J.S.; WANG, K.L.; MACWILLIAMS, K.P., *Appl. Phys. Lett.* 62 (1993) 2853-2855.
4. WELSER, J.; HOYT, J.L.; GIBBONS, J.F., *IEEE Trans. Electron Devices* 40 (1993) 2101.
5. MURAKA, S.P.; *J. Vac. Sci. Technol., B* 4 (1986) 1325-1331.
6. D'HEURLE, F.M., *J. Mater. Res.* 3 (1988) 167-195.
7. NYGREN, S.; CAFFIN, D.; OSTLING, M.; D'HEURLE, F.M., *Appl. Surf. Sci*. 53 (1991) 87-91.
8. MANGELINCK, D.; GAS, P.; GAY, J.M.; PICHAUD, B.; THOMAS, O., *J. Appl. Phys.* 84 (1998) 2583-2590.
9. LEE, P.S.; PEY, K.L.; MANGELINCK, D.; DING, J.; OSIPOWICZ, T.; SEE, A., *Electrochem. Solid-State Lett*. 5 (2002) G15-G17.
10. HELLBERG, P.-E.; ZHANG, S.-L.; PETERSSON, C.S., *IEEE Electron Device Lett.* 18 (1997) 456-458.

11. GANNAVARAM, S.; PESOVIC, N.; OZTURK, M.C., *Tech. Dig.-Int. Elect. Devices Meet*. (2000) 437-440.
12. SEGER, J.; ZHANG, S.-L.; MANGELINCK, D.; RADAMSON, H.H., *Appl. Phys. Lett,* 81 (2002) 1978-1980.
13. LIU, J.F.; CHEN, H.B.; FENG, J.Y.; ZHU, J., *Applied Physics Letters* 77 (2000) 2177-2179.