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AlN bulk crystals grown on SiC seeds

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Abstract

AlN layers with thickness between 0.1 and 3 mm were grown on on-axis and off-axis (0 0 0 1), Si-face SiC seeds by physical vapor transport (PVT) from an AlN powder source. A two-step deposition process was developed for the growth of thick layers. Cracks formed in the AlN layers due to the thermal expansion mismatch between AlN and SiC were observed to decrease with increase in AlN thickness. AlN grown on on-axis SiC was primarily Al-polar, but contained N-polar inversion domains (IDs) revealed by wet etching in hot, aqueous phosphoric acid or potassium hydroxide solutions. Regions of opposite polarity on basal plane surfaces were imaged by piezoresponse force microscopy (PFM). IDs were not observed in crystals grown on off-axis seeds. The influence of SiC seed orientation and stability on the polarity of the AlN layers is discussed.

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1. Introduction

The wide bandgap group-III nitrides have been identified as promising materials for applications in electronic and optoelectronic devices [1]. Considerable progress has been achieved in thin film growth of these materials, and devices such as blue light-emitting diodes are commercially available. However, substrate technology remains a critical issue for the improvement of nitride devices. Currently, devices grown on non-native substrates, such as sapphire and SiC, contain a large density of defects, which limits device performance and lifetime. Defect structures identified in heteroepitaxially grown nitride thin films include threading dislocations, stacking faults, nanopipes, and inversion domains (IDs). Due to its close lattice match with AlGaN, similar coefficient of thermal expansion, wide bandgap, high thermal conductivity, and high chemical and thermal stability, single crystal AlN is an excellent candidate as a III-nitride substrate material [2]. Bulk AlN crystals

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grown by the sublimation–recondensation technique have been reported [3,4], but presently, large AlN single crystals are still not available in large quantities. Seeded growth of AlN on SiC has been studied by a number of groups [5–7] as a way to exploit the availability of large, high-quality SiC substrates and to control the polarity and orientation of AlN crystals. Due to the high process temperatures involved in this technique, and the difference in thermal expansion coefficient between AlN and SiC, the stability of the SiC seeds and the cracking of the AlN layers are important issues that need to be addressed in establishing a reproducible seeded growth process. Shi et al. [6] have reported a technique for reducing cracks in the AlN by first depositing an $(\mathrm{AlN})_x(\mathrm{SiC})_{1-x}$ alloy layer prior to sublimation growth of pure AlN; single-crystal AlN platelets 4 × 6 mm and 0.5 mm thick were obtained. In this paper, we describe a process that was developed for deposition of thick AlN layers on SiC, and for reduction of cracks in the grown layers. The influence of SiC seed orientation on the polarity and morphology of the AlN layers will be discussed. In addition, we report on the observation of polar defect structures in AlN grown on on-axis SiC that will be identified as IDs.

The AlN hexagonal wurtzite structure is composed of two interpenetrating hexagonal close-packed cation and anion sublattices displaced by 1.917 Å along the *c*-axis that contain Al and N atoms in tetrahedral coordination [8]. This is a non-centrosymmetric structure, and thus AlN possesses different properties along different $\langle 0001 \rangle$ polar directions. The polarity of AlN can be defined with respect to the position of the Al atom in the $\{0001\}$ bilayer [1]. In Al-face $(+c)$ AlN, the Al atom occupies the top position in the bilayer, while in N-face $(-c)$ AlN the top position is occupied by N, corresponding to filling by Al of either upward-pointing or downward-pointing tetrahedral sites. By convention the crystallographic [0001] axis points from the N-face to the Al-face. IDs have been studied in AlN sintered ceramics [8,9] and in thin films grown by metal organic chemical vapor deposition (MOCVD) on sapphire substrates [10,11], and models of the domain wall structure have been formulated. The different response to etching of $+c$ and $-c$ polar $\{0001\}$ nitride surfaces has been observed in thin films and bulk crystals of GaN and AlN [12–15], and can be used to identify defects such as IDs on these surfaces.

Piezoresponse force microscopy (PFM) has been used to image domain structure in ferroelectric thin films [16] and lateral polarity heterostructures in GaN films [17] with nanometer-scale spatial resolution. In this scanning probe microscopy (SPM)-based technique, a modulating voltage is applied to a conducting tip in mechanical contact with a piezoelectric sample. The magnitude and phase of the bias-induced tip deflection, which follows the piezoelectric motion of the sample surface, are used to determine the piezoelectric coefficient d_{33} and the polarity of the sample. The tip can be rastered over the surface to create two-dimensional images of the piezoresponse signal. Since the sign of the piezoelectric coefficient depends on the polarization direction, the sample will oscillate either in-phase or out-of-phase with the applied voltage. In the wurtzite III-nitrides the spontaneous polarization points from the III-metal atom face to the N-face. Thus, in Al-face AlN the oscillation is in-phase with the modulating voltage, while in N-face AlN the oscillation is out-of-phase; regions of different polarity exhibit opposite contrast in a PFM phase image, with the N-face polarity appearing brighter [17]. Due to the capability to image regions of different polarity, PFM is well suited to study IDs in the III-nitrides and can be used to confirm the trends observed in etching studies.

2. Experiment

As shown schematically in Fig. 1, an AlN crystal growth process similar to the sandwich sublimation process for growth of SiC was employed in these studies. Crystal growth was performed in a dedicated reactor equipped with a cylindrical graphite heater capable of temperatures in excess of 2200 °C. The growth apparatus has been described elsewhere [4]. Several grams of commercially purchased AlN powder (7–10 μm) were loaded into the bottom of a sintered TaN crucible,

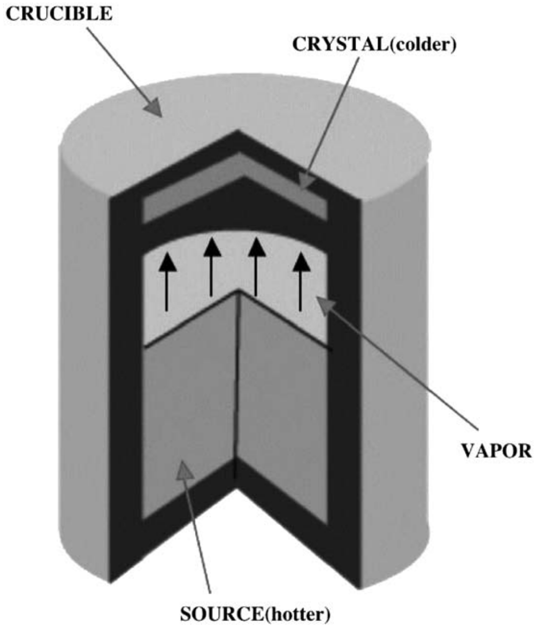

Fig. 1. Schematic of the AlN crystal growth process; AlN powder source sublimes and re-condenses on a colder seed crystal.

6–7 cm high and with a 2.5 cm inner diameter. Glow discharge mass spectrometry (GDMS) indicated that the as-received AlN powder contained approximately 0.3 wt% carbon, 0.1 wt% oxygen, and 0.1 wt% other impurities, primarily metallic impurities. It was found that sintering of the source powder prior to crystal growth resulted in a significant reduction of nearly all impurities [18]; results reported below were obtained using both as-received and pre-sintered source powder. Physical vapor transport (PVT) growth was driven by a temperature gradient between source (hotter) and seed (colder). The vertical position of the crucible relative to the graphite heater was adjusted in order to control the temperature gradient over a range of 1–3 °C/mm. AlN was deposited on the SiC seeds at temperatures between 1850–2000 °C.

SiC seeds were obtained from commercial vendors. Two-inch substrates were used as-received or with a 200–400 nm AlN epilayer deposited by MOCVD. The epilayer was intended to promote two-dimensional nucleation of AlN [6]. In order to investigate the influence of substrate orientation on the growth and morphology of AlN, experiments were performed on both on-axis and 4° off-axis (0 0 0 1) oriented, Si-face 6H-SiC, and 8° off-axis (0 0 0 1) oriented, Si-face 4H-SiC substrates. As-received substrates were pre-treated in 25% HF solution at room temperature for 3 min and rinsed in de-ionized water prior to loading; substrates coated with an AlN epilayer received no additional pre-treatment.

High-resolution X-ray diffraction was performed using a Bede D1 high-resolution diffractometer system with Cu $K_{\alpha 1}$ radiation. Crystal morphology was studied by electron microscopy using a Hitachi S-3200 scanning electron microscope operated at 5 kV accelerating voltage, and by optical microscopy. Chemical composition of the crystals was analyzed by GDMS (VG 9000). PFM measurements were obtained with a TM Microscopes AutoProbe M5 equipped with conducting cantilevers (force constant 2.1 N/m) and a dual-phase lock-in amplifier (SR 830). A 1000 Å layer of 0.1 Ω cm p-type diamond was deposited on the cantilever Si tips.

3. Results

AlN layers ranging in thickness from 0.1 to 3 mm were grown via a two-step process on on-axis seeds coated with an MOCVD AlN epilayer (Fig. 2). During the first stage of growth, a coalesced layer of AlN is deposited over the entire surface of the seed at a moderate temperature (typically < 1900 °C), yielding growth rates between 10 and 30 μm/h. After a sufficient amount of time to form a fully coalesced layer, the temperature is slowly raised 100–200 °C, in order to deposit AlN at higher growth rates, approximately 70 μm/h. As-grown surfaces were characterized by sharp hexagonal hillocks, similar to those observed by Epelbaum et al. [7]. High-resolution rocking curves of the (0 0 0 2) reflection showed FWHM ranging from 456–1440 arcsec, indicating a tilt distribution in the grown layers probably caused by the formation of subgrain boundaries as the hexagonal hillocks coalesced. In samples where a fully coalesced layer was not

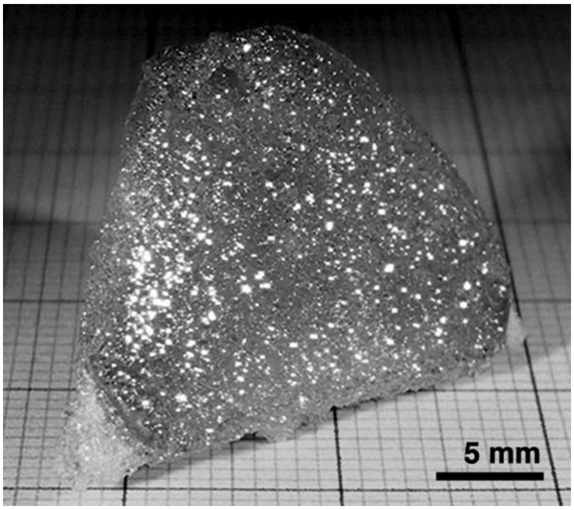

Fig. 2. 2.5 mm thick AlN crystal grown on on-axis 6H-SiC. During high-temperature growth, the seed almost completely evaporated. No cracks were observed in the AlN.

deposited during the first growth stage, voids were observed in the AlN. Cross sections taken from 2 mm thick samples indicated that voids were concentrated in the vicinity of the seed interface and that voids were typically overgrown by AlN after 1 mm of growth. Holes were observed in the AlN where overgrowth did not occur. Cracks were always observed in layers less than 1 mm thick. However, crack-free crystals were obtained from thicker layers (>2 mm) and these crystals were used to prepare polished wafers (Fig. 3) with ~1 nm RMS roughness as determined by atomic force microscopy (AFM). GDMS indicated oxygen, carbon, and silicon contamination levels in the range of 500–1200, 160–300, and 130–200 ppm wt, respectively.

AlN grown on as-received off-axis seeds exhibited two distinct morphologies: flat regions with ~100 μm-wide terraces characteristic of step-flow growth, and rough regions containing large, millimeter-wide hexagonal hillocks. The AlN exhibited a sharp interface with the SiC seeds and voids were not observed in the grown layers.

Crystals grown on both on-axis and off-axis seeds were etched in aqueous solutions of phosphoric acid (40%) and potassium hydroxide (6 M) at 60 °C for 5–30 min in order to determine their polarity. The as-grown (0 0 0 1) surfaces of crystals grown on off-axis seeds showed no etching for any of the etch times or solutions studied. Furthermore, crystals that were removed from the SiC seeds, either by delaminating them or by grinding off the seed, were evenly etched on the side facing the seeds. By contrast to these samples grown on off-axis seeds, polished wafers prepared from thick AlN layers grown on on-axis (0 0 0 1) SiC seeds contained 50–200 μm-wide regions of etched hexagonal hillocks. One such region, confined within a smooth surface, is shown in Fig. 4.

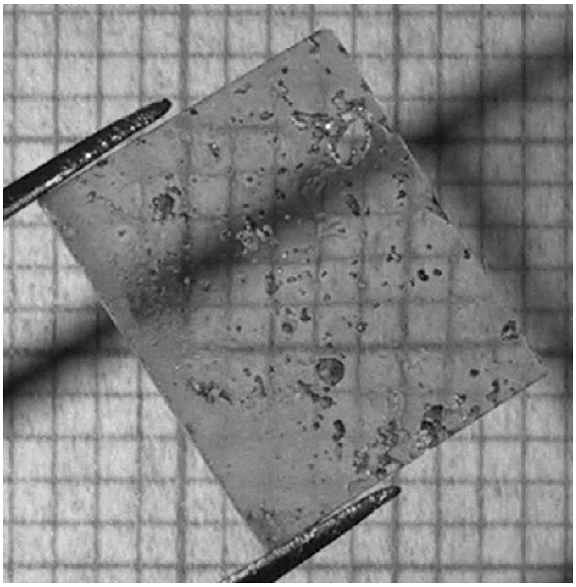

Fig. 3. AlN wafer, 9 × 11 mm, 500 μm thick, prepared from bulk AlN grown on on-axis 6H-SiC (mm grid). Dark spots are from incomplete polishing on the wafer back side.

4. Discussion

The growth mode of AlN deposited by sublimation on SiC has been studied by Liu et al. [6], who found that growth on as-received, on-axis or off-axis SiC seeds proceeded in an island mode promoted by screw dislocations. An AlN epilayer deposited on the seeds prior to sublimation growth was employed to change the growth mode to layer-by-layer growth. In our experiments on AlN-coated on-axis seeds it was found that

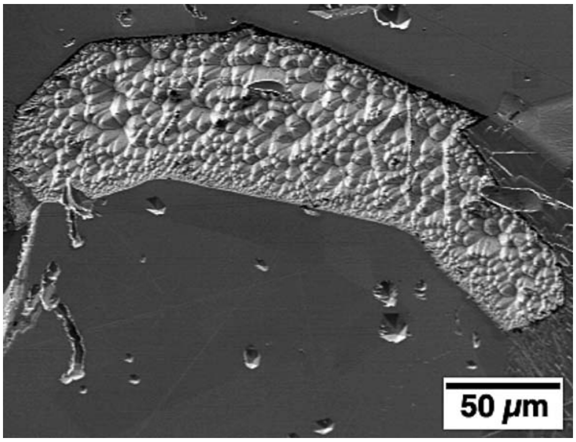

Fig. 4. Hillocks revealed in a N-polar ID on an Al-polar surface by etching in KOH solution at 60 °C for 10 min.

two-dimensional growth could only be sustained for thinner layers, below approximately 300 μm. With increasing AlN thickness the surface morphology changed from smooth to rough. Hexagonal hillocks and growth spirals were observed, indicating a dislocation-mediated island growth mode. In addition, it was found that SiC seeds were highly sensitive to the growth temperature. Premature decomposition of the seed surface led to the formation of voids in the AlN. Seeded growth requires a delicate balance between the need to preserve the integrity of the SiC seeds and the need to deposit bulk AlN at sufficiently high growth rates to obtain thick layers. For this reason, a two-step growth process was developed. During the low-temperature stage, a fully coalesced AlN nucleation layer that could sustain subsequent growth was deposited on the seed surface. The temperature was selected such that decomposition of the seed surface was minimized. In order to increase the growth rate of AlN, the temperature was then slowly raised. Growth proceeded on the AlN nucleation layer despite the gradual decomposition of the SiC substrate. Elimination of the SiC substrate over the course of the growth was beneficial for the production of crack-free crystals, since the AlN was no longer strained during cool down by the thermal expansion mismatch with the seed. GDMS results confirmed that crystals grown by this method contained at most 300 ppm wt C and 200 ppm wt Si, values comparable to those found in the AlN source powder, indicating negligible incorporation of C and Si during growth.

Previous reports indicated that AlN grown on Si-face SiC should grow with the Al-polar face [14]. The polarity of AlN can be determined by wet etching since the Al-face is more stable than the N-face in either phosphoric acid or potassium hydroxide solutions [14,15]. No etching was observed on the as-grown (0 0 0 1) surfaces of AlN deposited on off-axis seeds, which are thus identified as Al-polar surfaces. Since etching was observed on the side of the crystals facing the seed, this is identified as the N-polar face. These observations are consistent with the expected orientation of AlN grown on Si-face SiC. The etching results observed in Fig. 4, however, are consistent with the presence of N-polar IDs in a smooth Al-polar surface. Thus, AlN grown on on-axis SiC remained primarily Al-polar, but contained N-polar IDs up to 200 μm in width. Observation of the opposite face of these crystals (i.e. the side facing the SiC seed) revealed an etched N-polar surface, which contained corresponding, smooth Al-polar regions, thus indicating that these IDs typically propagated through the entire crystal. However, the surface area covered by N-polar regions on the top face was smaller than the extent of Al-polar areas observed on the side facing the seed; it appears that some of the IDs may have been overgrown by Al-polar material. The location of these IDs typically coincides with the presence of underlying voids at the interface with the SiC, which were subsequently overgrown by AlN. However, the nucleation mechanism of these IDs is still unclear. They may be formed in the MOCVD AlN epilayer itself and then propagate into the subsequently deposited PVT layer. This would account for their being observed only in layers grown on on-axis seeds with an AlN epilayer, but has not been confirmed. A model [8,9] for the inversion domain boundary structure has been formulated and verified for IDs observed in sintered ceramics, where an increase in the oxygen concentration of the AlN lattice beyond a critical value (~5850 ppm wt) results in a stabilized domain boundary consisting of Al atoms octahedrally bonded to oxygen atoms. However, oxygen impurities in our AlN crystals measured by GDMS are at levels (~500–1200 ppm wt) significantly below the critical value in this model. It is also possible that when voids are formed at the AlN/SiC interface, the AlN overgrown at a later stage does not replicate the polarity of the substrate. This may explain why IDs were not observed in AlN grown on off-axis seeds; these interfaces were typically continuous, due to enhanced lateral growth from step flow.

In order to confirm the presence of IDs inferred from the etching results, polished crystals were imaged by PFM. Fig. 5(a) shows an optical microscopy image of a polished feature that exhibited an etching response similar to Fig. 4. The edge contrast is due to the difference in height between the polished surfaces of opposite polarity. It was observed that N-polar regions were polished more deeply than the surrounding Al-polar material, which is a reflection of the greater instability of the N-face. This surface relief is confirmed in the PFM topography image (Fig. 5(b)). The fact that the observed features are indeed IDs is unambiguously demonstrated in the PFM phase image (Fig. 5(d)). Regions of different polarity exhibit opposite contrast, and the N-polar region identified by etching is brighter, as expected.

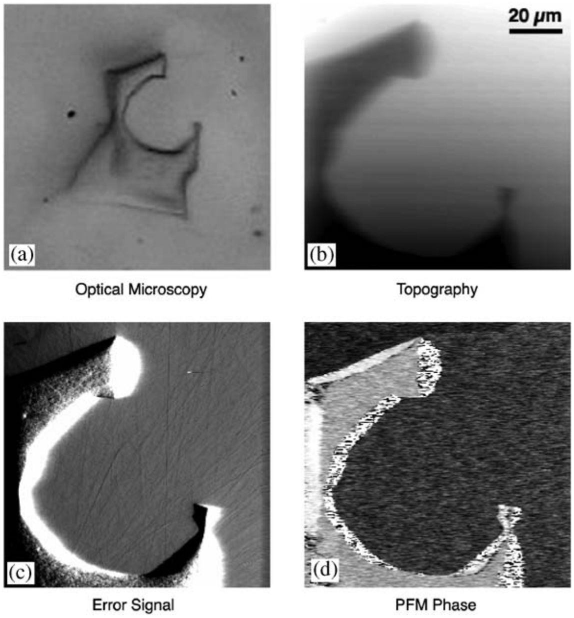

Fig. 5. (a) Optical microscopy image of a N-polar ID on an Al-polar AlN surface after polishing; (b) PFM topography image indicating surface relief (vertical scale: 800 nm); (c) PFM error signal (vertical scale: 60 nm). Surface scratches are visible on the polished Al-polar surface (~2 nm RMS roughness); (d) PFM phase image indicating opposite contrast between N-polar (brighter) and Al-polar regions.

5. Conclusions

A two-step process was developed for growth of AlN bulk crystals on SiC seeds. AlN layers up to 3 mm thick were grown by PVT on on-axis and off-axis (0 0 0 1) Si-face SiC seeds. Crack-free AlN crystals were obtained from these layers. Growth temperature, as well as SiC substrate orientation, was found to influence the morphology of the AlN layers. The stability of the SiC seeds was highly sensitive to temperature. Below 1900 °C, coalesced AlN layers were obtained on both on-axis and off-axis seeds, while growth above this temperature resulted in premature decomposition of the SiC and incomplete coalescence of the initial nucleation layer. The subsequent growth behavior depended strongly on the formation of a coalesced nucleation layer. Voids and holes were observed in the AlN as a consequence of premature seed decomposition. Finally, IDs were observed in AlN grown on on-axis seeds coated with an MOCVD AlN epilayer. Further investigation is required to determine the nucleation mechanism of the IDs. These defects have not been observed in AlN grown on as-received off-axis SiC.

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References

[1] O. Ambacher, J. Phys. D: Appl. Phys. 31 (1998) 2653.

[2] L. Liu, Y. Shi, J.H. Edgar, MRS Internet J. Nitride Semicond. Res. 6 (2001) 7.

[3] B. Raghothamachar, M. Dudley, K. Morgan, L.J. Schowalter, J. Crystal Growth 250 (2003) 244.

[4] R. Schlesser, R. Dalmau, Z. Sitar, J. Crystal Growth 241 (2002) 416.

[5] C.M. Balkas, Z. Sitar, T. Zheleva, L. Bergman, R. Nemanich, R.F. Davis, J. Crystal Growth 179 (1997) 363.

[6] Y. Shi, B. Liu, J.H. Edgar, E.A. Payzant, J.M. Hayes, M. Kuball, MRS Internet J. Nitride Semicond. Res. 6 (2001) 5.

[7] B.M. Epelbaum, M. Bickermann, A. Winnacker, Mater. Sci. Forum 433–436 (2003) 983.

[8] A.D. Westwood, M.R. Notis, J. Am. Ceram. Soc. 74 (1991) 1226.

[9] A.D. Westwood, R.A. Youngman, M.R. McCartney, A.N. Cormack, M.R. Notis, J. Mater. Res. 10 (1995) 1270.

[10] J. Jasinski, T. Tomaszewicz, Z. Liliental-Weber, Q.S. Paduano, D.W. Weyburne, Mater. Res. Soc. Symp. Proc. 798 (2004) Y5.29.1.

[11] J. Jasinski, Z. Liliental-Weber, Q.S. Paduano, D.W. Weyburne, Appl. Phys. Lett. 83 (2003) 2811.

[12] J.L. Rouvière, J.L. Weyher, M. Seelmann-Eggebert, S. Porowski, Appl. Phys. Lett. 73 (1998) 668.

[13] J.L. Weyher, P.D. Brown, J.L. Rouvière, T. Wosinski, A.R.A. Zaurer, I. Grzegory, J. Crystal Growth 210 (2000) 151.

[14] D. Zhuang, J.H. Edgar, L. Liu, B. Liu, L. Walker, MRS Internet J. Nitride Semicond. Res. 7 (2002) 4.

[15] D. Zhuang, J.H. Edgar, B. Strojek, J. Chaudhuri, Z. Rek, J. Crystal Growth 262 (2004) 89.

[16] S.V. Kalinin, D.A. Bonnell, Phys. Rev. B 65 (2002) 125408.

[17] B.J. Rodriguez, A. Gruverman, A.I. Kingon, R.J. Nemanich, Appl. Phys. Lett. 80 (22) (2002) 4166.

[18] R. Dalmau, B. Raghothamachar, M. Dudley, R. Schlesser, Z. Sitar, Mat. Res. Soc. Symp. Proc. 798 (2004) Y2.9.1.